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Pulsed Thermo Kinetic (PTK) Measurements

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A novel technique, pulsed thermo kinetics (PTK), for studies in catalysis has been developed. A pulsed microreactor and conventional DTA apparatus were combined to yield stimultaneous thermal and concentration peaks for a pulse of reactant or adsorbate passing over a catalyst. The method of measurement, calibration and complications are described. Possible applications to catalysis are discussed.

INTRODUCTION

One useful phase of catalysis research is the development of techniques that are rapid and simple yet yield results applicable to more realistic conditions. Such a technique is the pulsed micro-reactor (*1*). Although transient in nature, and thus unsuited for simple kinetic studies, the pulsed reactor has nevertheless proven to be a valuable tool for rapid catalyst screening (*2*), poison titrations (*3*), and surface mechanism studies (*4*). We have developed a similar technique by combining a pulsed reactor with a heat-flow microcalorimeter (*5*). Thus we are able to obtain both kinetic-related data and thermal information as a pulse of adsorbate or reactant passes over the catalyst bed and adsorbs or reacts. For this reason we have called the method the pulsed thermo kinetic (PTK) technique.

The principal difference between PTK and heat-flow calorimetric measurements is the introduction of the pulse, but this provides advantages. The PTK system is a dynamic flow rather than a static arrangement. This allows the study of both adsorption and reaction in packed beds. With the additional data from the pulsed microreactor, both the extent of conversion and the heat of reaction (or adsorption) are simultaneously measured. Also, since the pulse is a transient it is possible to uncouple the effects of adsorption and reaction to yield information not provided by other methods. The transient nature of the mass and heat flows do, however, introduce complications to the analysis, but these are not beyond control.

The PTK method has been applied in this laboratory to studies in adsorption and reactions (*6*). This paper describes the method and associated problems. Subsequent papers will concentrate on applications.

APPARATUS

The apparatus used in the PTK measurements is a modified differential thermal analysis (DTA) instrument. The arrangement is shown in Fig. 1. The gas inlet system consists of appropriate flow regulating and measuring components. The carrier gas may be either helium or hydrogen, with the sample stream of adsorbate or reactant passing through the pulsing valve for subsequent injection into the carrier stream.

Details of a simple PTK differential reactor cell are shown in Fig. 2. Two stainless steel tubes, 0.25 in. o.d. are forced through a brass block, as shown, and con-

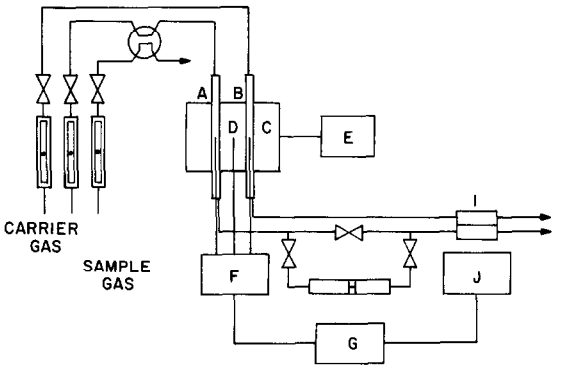

FIG. 1. Apparatus for PTK measurements (A) sample cell; (B) reference cell; (C) heater block; (D) thermocouples; (E) temperature control; (F) ΔT amplifier; (G) dual-point recorder; (H) chromatographic column; (I) thermal conductivity cell; (J) bridge control.

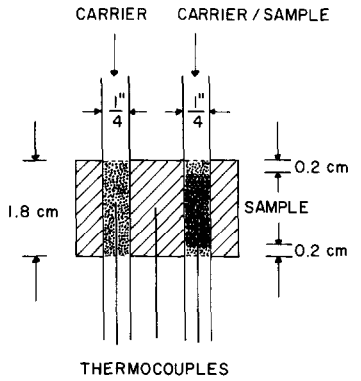

FIG. 2. PTK cell.

nected with Swagelok fittings to the reference and sample carrier streams. The catalyst under investigation is packed into the sample side of the cell and a reference material with the same thermal conductivity into the other side. Since only the sample side is pulsed with adsorbate or reactant, the reference material may very well be the catalyst itself.

A thermocouple in the block serves to measure and control the temperature. Thermocouples in the sample and reference streams are connected differentially to record time-dependent differences in temperature between sample and reference as the pulse passes through the bed.

Instrumentation for control and measurement is provided by a conventional DTA apparatus (Tracor, DTA-202), which features a linear temperature programmer, a dc amplifier for the differential thermocouple assembly and a dual pen recorder. The differential reactor block is sized to fit the Tracor furnace assembly.

One channel of the recorder is used to record the differential thermal peak associated with the pulse. The other channel records the output of the thermal conductivity cell (Gow-Mac) used to analyze the effluent pulse. Thus simultaneous concentration and thermal peaks are obtained.

In cases where the reactant pulse converts into other components, an appropriate chromatographic column may be switched into the sample stream between the reactor and the thermal conductivity cell. In this configuration, the thermal peak is accompanied by a chromatogram for conversion analysis.

In typical applications we have used a commercial nickel catalyst (0.200 g, 250–350 μm) sandwiched between two layers of 0.07 g, 60 mesh alpha-alumina. After reduction at 375°C in hydrogen, the catalyst was studied over a range of temperatures for hydrogen/ethylene adsorption and ethylene hydrogenation. Flow rates up to several hundred millimeters per minutes were used. The results of these measurements will appear in a subsequent paper.

The temperature programming feature of

the commercial DTA provides a bonus. In addition to PTK adsorption measurements, the apparatus may be used to carry out a temperature programmed desorption (TPD) study (*7*).

TYPICAL RESULTS

Typical results are shown in Figs. 3 and 4. The peak in Fig. 3 is an exothermic response when a pulse of ethylene is reacted into a stream of hydrogen passing over a nickel catalyst at 25°C. It will be shown later that the area under the peak is proportional to the heat evolved. Thus, with the degree of conversion given by the associated chromatogram, the heat of reaction per mole of ethylene reacted may be easily determined.

When a pulse of hydrogen is injected into the carrier stream (helium or argon) passing over a freshly reduced and cleaned (He at 400°C) nickel surface, an exothermic peak similar to that in Fig. 3 is the result. This initial hydrogen is rapidly and irreversibly adsorbed so that the thermal peak represents the initial heat of adsorption of this mode.

With each successive pulse, the area of the peak becomes smaller. When all the sites for irreversible adsorption are filled, the exothermic peak is followed by an endothermic peak, shown in Fig. 4. When the irreversible sites are fully saturated the areas of the two peaks are the same.

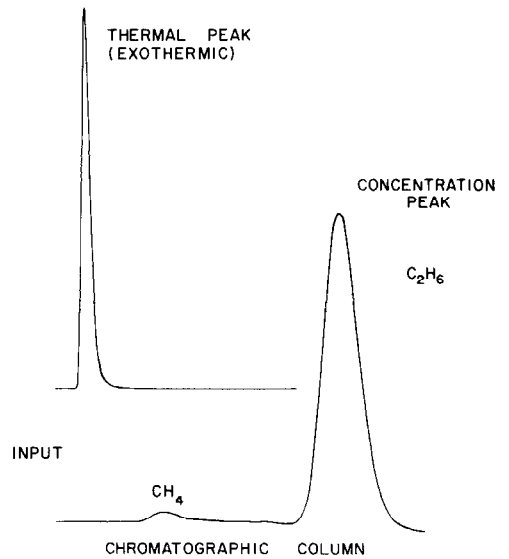

FIG. 3. Typical PTK peak for an exothermic reaction.

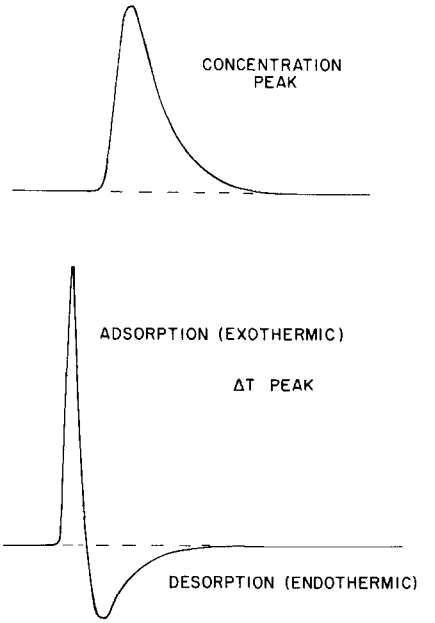

FIG. 4. Typical PTK peaks showing the exothermic adsorption peak and the endothermic desorption peak for hydrogen.

This type of thermal response is representative of reversible adsorption where the adsorption occurs rapidly but the desorption, corresponding to the endothermic peak, is much slower. Since this is usually the situation this type of peak is quite typical of reversible adsorption. The greater the difference between the rates of adsorption and desorption, the better the resolution between the exothermic and endothermic peaks. The areas themselves are not truly indicative of the heats involved unless this resolution is well defined. If overlap exists, the areas will be accordingly reduced. Even for the best resolution, a quantitative estimation of the heat of adsorption would necessitate a knowledge of the total adsorption–desorption acts involved. Nevertheless, these results

yield valuable quantitative information of the relative rates of adsorption–desorption.

It should be pointed out that for the resolution of peaks such as these in Fig. 4, low time constants for the thermocouples are necessary. If these time constants are long compared with the time of the pulse, then the exothermic and endothermic heats will be combined or overlap to a much greater extent. We have found that time constants of about half the pulse time (10–30 sec) are necessary for the best results. These observations are only critical if precise interpretation of the shapes of exothermic and endothermic peaks are to be attempted. In most cases, where only one type of heat is involved, it is sometimes advantageous to risk the higher time constant of, for example, a shielded thermocouple, in return for electrical isolation, stability, etc. Each individual application must be considered when designing the appropriate system.

CALIBRATION

In order to interpret the peak areas in terms of the quantity of heat involved, it is necessary to know the mechanism for heat transfer away from the bed. Two types are possible: conduction from the reaction zone to the block around the bed and convection by the reactant-carrier stream down from the bed. Conduction is the usual mode in DTA cells and calculations show that it should be dominant under the flow conditions used in these PTK measurements. Nevertheless, we performed the following experiments to confirm conduction.

Pulses containing 6.7×10^{-6} moles of oxygen were pulsed into a helium stream passing over a 0.4 cm bed of 0.07 gm nickel catalyst. In two separate runs, the thermocouple was positioned outside of, but touching, first the front of the bed and secondly the back of the bed. The results are shown in Fig. 5.

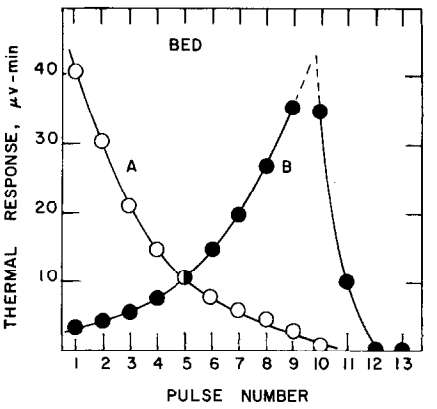

FIG. 5. Zoning effects with O_2 adsorption.

The decrease in Curve A and the increase in Curve B clearly indicate that zoning is taking place, that is, the oxygen is adsorbing rapidly to fill all available nickel sites first in the very front of the bed and then subsequently down the bed with each progressive pulse. The symmetry of Curves A and B, however, shows that the heat transfer mechanism must be occurring through the catalyst to the thermocouple, with the amount of heat reaching the thermocouple proportional to the distance between it and the adsorption zone, independent of the direction of gas flow. This is then conduction. If convection were a major factor, the curves would be asymmetrical. Indeed, a very sharp drop off would occur for zones downstream from the thermocouple with a constant response for zones upstream.

We have confirmed these conclusions with many experiments at different flow rates with none of the results to be expected for convection flow.

Under these conditions the simple expression applicable to DTA may be used (*8*), namely

$$A = \frac{G \cdot \Delta H}{\lambda_e} \qquad (1)$$

where A is the area of the curve, ΔH is the heat evolved, λ_e is the effective thermal conductivity of the reaction system, and G is the instrumental constant.

Equation (1) is an approximation only which neglects temperature gradients in the sample and considers the peak area to be independent of specific heat of the sample. Nevertheless, it has been found to be directly applicable to PTK measurements with the following modification.

The effective thermal conductivity, λ_e, will change with the nature of the carrier gas filling the void space of the bed. Thus, calibrations made in one gas would need correction for use in another. In order to implement this correction, we use the approximation

$$\lambda_e = (1 - \epsilon)\lambda_c + \epsilon\lambda_g \qquad (2)$$

where λ_c is the thermal conductivity of the catalyst, λ_g is the thermal conductivity of the carrier gas, ϵ is the void fraction of the catalyst bed. Equation (2) then becomes

$$A = \frac{G \cdot \Delta H}{(1 - \epsilon)\lambda_e + \epsilon\lambda_g} \qquad (3)$$

Equation (3) was checked by pulsing ethylene into a carrier mixture of H_2–Ar. The ethylene was completely reacted so that ΔH remained constant. By changing the H_2/Ar ratio, the carrier conductivity, λ_c, could be varied.

Figure 6 shows a plot of $1/A$ vs λ_c. Clearly Eq. (3) is followed under these conditions. The intercept is related to λ_c, which calculates to be 0.58×10^{-3} cal/(cm · sec · °C). This is a reasonable value for the catalyst under investigation.

Plots such as Fig. 6 must be used to correct the calibration for changes in carrier gas and temperature. We have not attempted to correct for the thermal conductivity of the material in the pulse since in most cases the heat flow will lag the passage of the material pulse.

However, when a pulse of a gas with a different thermal conductivity from the carrier gas passes through the cell, the local change in conductivity modifies the heat flux from the surroundings to the thermocouple. This effect (similar to that experienced in thermal conductivity cells) is proportional to

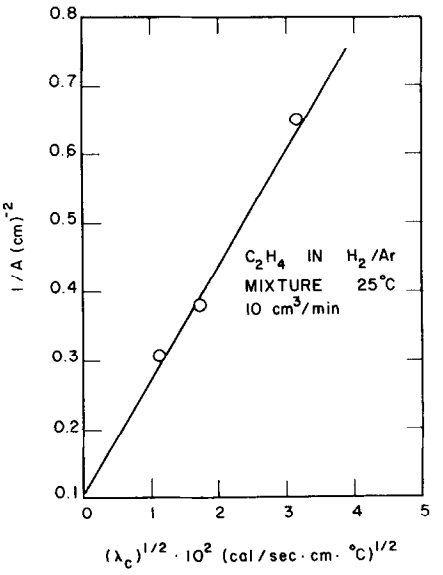

FIG. 6. Effect of carrier gas thermal conductivity on thermocouple response.

$$\frac{\lambda_g - \lambda_s}{\lambda_c}, \qquad (4)$$

where λ_s is the thermal conductivity of the sample.

Thus, except for room temperature (zero heat flux), a spurious peak will result. It is expected that this peak will increase with conductivity difference and temperature but decrease with flow rate. To determine the magnitude of this effect, we pulsed gases with various thermal conductivities into the helium carrier gas and through a bed of inert α-Al_2O_3 at various temperatures and flow rates. The results, shown in Fig. 7, confirm the expectations but the observed peaks were only a few percent of those observed in most of our measurements. However, it is necessary when measuring very small peaks to apply corrections based on measurements similar to those shown in Fig. 7.

Calibration of the instrumental factor is best achieved experimentally. It is possible to input a known pulse of heat by means of

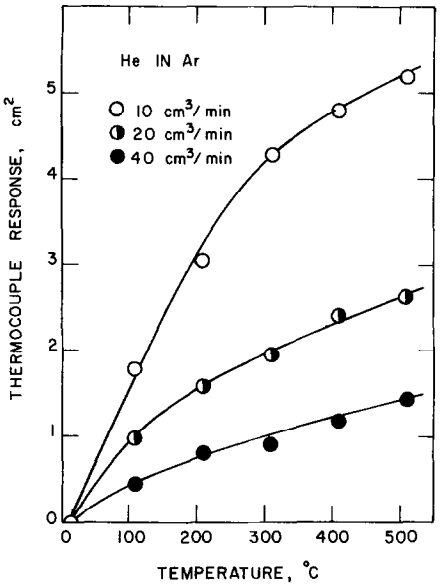

FIG. 7. Effect of pulsed gas thermal conductivity on thermocouple response.

an internal electrical heater, as practiced in calorimetry. However, this approach is not convenient for this type of cell. It is far easier to carry out a catalytic reaction involving a known amount of heat release.

In the examples presented here, ethylene hydrogenation was used. However, great care must be taken to ensure that the reaction is not so rapid that zoning, such as in Fig. 5, occurs. The heat released should be uniform throughout the bed. For this reason, the calibration reaction should preferably be carried out with incomplete conversion and, if possible, at small conversions, to avoid concentration profiles in the bed. This requirement sometimes introduces serious sensitivity problems so that compromises must be made. Usually, if the size of the peaks is large compared to the bed, this problem can be minimized.

COMPLICATIONS

The most serious complication in data interpretation is that of zoning as mentioned in the discussion of calibration. If the reaction takes place in the front portion of the bed while the calibration was made throughout the bed, or vice versa, then obviously incorrect instrumental factors will be applied. In each case, tests must be conducted to ascertain whether or not zoning is taking place.

One method is to increase the flow rate. This will result in a larger reaction zone for conversion. Insensitivity of the heat evolved per mole of reactant consumed to flow rate is a fairly good indication of lack of zoning. Another, but more inconvenient, approach is to vary the position of the thermocouple. Zoning then becomes very obvious, as in Fig. 5.

If zoning is unavoidable, several corrective measures are possible. Data, such as that in Fig. 5, may be obtained and a calibration factor versus bed depth curve calculated. Application, however, requires a fairly good estimate of the position of the reaction zone. This method is, obviously, not the most reliable.

Another technique is to use more thermocouples. For instance, the combination of eight thermocouples smooths out the curves in Fig. 5 to an acceptable uniformity. However, this imposes severe fabrication problems in the design of a suitable bed.

Thermopiles external to the bed, as in heat flow calorimetry, is a possibility (*5*). These devices usually have larger time constants and would not be suitable where high resolution is desired.

We have had considerable success by enclosing the bed in a copper tube but insulating this from the brass block with glass. This forces heat down the bed, via the copper tube, and results in a fairly uniform response no matter where the reaction zone happens to be.

Once a suitable and workable calibration has been obtained, then the various corrections for temperature, thermal and conductivity, etc., must be applied.

Typical results with our apparatus result in peaks of 10.0 ± 0.2 $\mu V \cdot$ min for the complete hydrogenation of 5×10^{-6} moles

of ethylene at 25°C. Accuracy for overall measurement is 2–5% depending upon the size of the thermal response involved.

APPLICATIONS

Some applications of PTK measurements to catalysis are as follows:

1. Catalyst Screening

For catalyst screening purposes, the PTK method will yield thermal peaks that may be related to conversion and activity. An approach similar to this but using continuous flow has recently been described (*8*).

2. Adsorption

Heats of adsorption may be measured directly when irreversible adsorption occurs and exothermic peaks result. Provided zoning does not occur it is even possible to measure heat versus coverage by sequential pulsing.

Reversible adsorption is much more difficult. As discussed earlier, only in cases where the adsorption–desorption steps are resolved is meaningful interpretation possible. A greater insight may be obtained by combining PTK measurements with an analysis of the effluent peak shapes as discussed by Smith (*9*). This aspect will be explored in later papers.

3. Surface Reactions

The most promising application for PTK is in the study of surface reactions. By preadsorbing one reactant and pulsing with the other, it is possible to elucidate which surface species are reacting. With appropriate ingenuity, information may be obtained that is not possible by any other methods.

Specific details of these applications are given in the next paper in this series.

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