[CONTRIBUTION FROM MULTIPLE FELLOWSHIP OF GULF RESEARCH & DEVELOPMENT COMPANY, MELLON INSTITUTE]

An Improved Microcatalytic Technique

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An improved new microcatalytic technique, capable of yielding reproducible catalyst testing data, is outlined. Data describing the utility of the method in a kinetic study of the catalytic hydrogenation of ethylene are presented, and advantages of the technique over conventional methods are discussed.

In a recent communication from this Laboratory,[1] a new microcatalytic technique was outlined. This technique involved the injection of gaseous or liquid hydrocarbon reactants into a carrying gas stream which was passing over a catalyst and then directly through a chromatographic column. The products of the reaction were measured by the usual chromatographic technique, by attaching a thermal conductivity apparatus to the exit of the column and recording the peaks corresponding to the reaction products on a recording potentiometer. In this previous work, modified and unmodified hypodermic syringes were used for the hydrocarbon injection. The hypodermic needles were inserted into the carrying gas stream by pushing them through rubber serum caps. While this technique is probably adequate for many studies, it has two serious drawbacks: the first of these is that the reproducibility obtainable is limited by the accuracy by which gases and/or the extremely small samples of liquid can be measured and transferred in hypodermic syringes; a second limitation is encountered in studies over catalysts of reduced metals (particularly of fairly low surface areas) where oxygen diffusing in through the serum cap may irreversibly poison the catalyst. The technique described in the present paper circumvents both of these difficulties and in addition provides a means of preparing synthetic blends that may be used either in calibration or in the actual catalytic studies.

The equipment developed in the present work is shown schematically in Fig. 1; the doser device comprises the upper left-hand (blocked-in) corner and is shown there in relation to the remainder of the system. With the stopcocks in the position shown (3 is open and 4 is closed), the helium carrying gas is pushing the measured slug of reactant gas (8 cc. in these experiments) out from between the stopcocks toward the catalyst. In this situation, the by-pass stopcock for the carrying gas (4) is in the closed position. By reversing the doser stopcocks (1 and 2) by 180°, the by-passed stream of reactant gas could be run through the doser (close 3), while in turn, the helium carrying gas would be by-passed (open 4). Thus by proper manipulation, measured volumes of the flowing synthesis gas could be trapped between the doser stopcocks and in turn carried over the catalyst by the stream of carrying gas. The volume between the stopcocks, in which the gas is trapped, was calibrated gravimetrically with mercury before the doser device was sealed into the system. By an obvious modification, the doser volume may be varied by making this part of the assembly interchangeable.

Provision was also made for evacuation of the measured volume and the filling of it with gas blends of known composition from a gas buret attached to a manometric system as shown in Fig. 1. This feature was especially convenient in calibration.

As an example of the utility and reproducibility of this equipment, data will be presented below for an experiment in which a mixture of 60% hydrogen–40% ethylene was passed over a copper–nickel alloy catalyst. These data comprise part of a study which will be reported in more detail elsewhere.[2] The slug of the gas mixture had a volume of about 8 cc. (NTP); the total catalyst surface area in the reactor tube was the order of one square meter. The chromatographic column was made from a seven foot length of one quarter inch stainless steel tubing packed with high area charcoal (Pittsburgh Coke and Chemical "Type B"). It was connected to the glass part of the system by a Kovar seal.

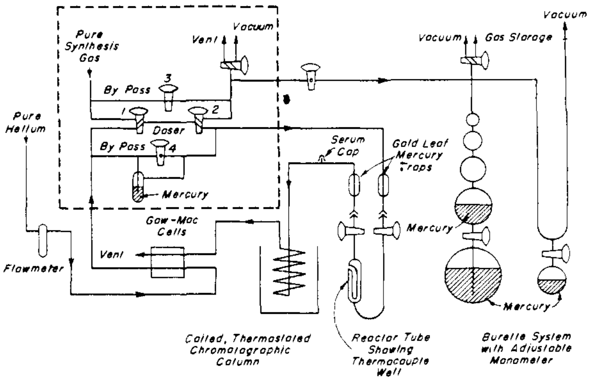

Fig. 1.—Flow sheet of microcatalytic system.

The column packing was accomplished by putting a plug of glass wool into one end of the straight piece so that the charcoal could be packed tightly into the column a little at a time while the tube was vigorously vibrated with an electric Vibra-tool. When the packing was completed, the upper end of the column was plugged with another piece of glass wool. The column was then formed into a coil which fit into a large Dewar flask where it was thermostated at 136°, using a conventional relay circuit. The exit end of the column was connected directly into the Gow–Mac thermal conductivity cell. It should be noted that the metered carrying gas passed through the other side of the Gow–Mac cell before reaching the doser.

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(2) W. K. Hall and P. H. Emmett, "The Hydrogenation of Ethylene Over Copper–Nickel Alloys," to be published.

An a.c. bridge circuit, developed and supplied by the Department of Instrumentation of the Mellon Institute, was used to link the output of the Gow–Mac cell to the unmodified Speedomax recording potentiometer. It proved to be both flexible and highly stable.

With reference to Fig. 1, the reactant gas was carried from the doser through the gold leaf mercury traps and over the catalyst. As the slug containing the reactant gases emerged from the catalyst, it passed directly over the charcoal chromatographic column and then through the Gow–Mac thermal conductivity cell.

The record obtained was, in effect, a plot of the concentration of hydrogen, ethylene and ethane passing out of the chromatographic column as a function of time. Quantitative measurements of the volume of the various components were obtained by integration of the peak areas using a planimeter. Calibrations to establish the area–volume relationships were made in several ways. First, ethylene and ethane were measured out separately or together in a hypodermic syringe and injected through the serum cap indicated in Fig. 1; the areas obtained from integration of the peaks obtained on the Speedomax record were plotted as abscissas against the volumes of gas injected as ordinates. Second, various gases of known compositions were used to fill the doser and the data obtained when these slugs were carried through the column were plotted on the same graph. The data obtained by both methods served to define two straight lines characterized by the slopes S_1 and S_2 when the areas obtained were plotted against the volumes introduced (as ordinates), one for ethylene and one for ethane. The scatter in the points obtained using the doser was considerably less than for those obtained with the hypodermic syringe. Data obtained by the former method deviated from the calibration curve by as much as 5% and occasionally a bit more, whereas in no case was a deviation of more than 2% observed with the doser method.

Defining the linear volume–area relationships established in the calibrations as S_1 and S_2 (as noted above) for ethylene and ethane, respectively, and defining similarly the areas produced in the analysis of a given mixture as A_1 and A_2, it is possible to write for the fraction ethane, r, in the mixture

$$r = S_2A_2/(S_1A_1 + S_2A_2) = A_2/[(S_1/S_2)A_1 + A_2] \quad (1)$$

When the doser is filled with a mixture of hydrogen and ethylene, and this slug is passed over the catalyst and partially converted, the percentage of ethane in the ethylene plus ethane mixture is a measure of the reaction rate. Thus equation 1 defines the reaction rate, r, which is sought. The ratio of the slopes of the volume–area calibration curves, S_1 to S_2, was found to be 1.012. It should be noted that this ratio would be expected to be less sensitive to uncontrolled external variables such as room temperature, atmospheric pressure, etc., than either S_1 or S_2 separately. It was found, however, that the calibrations were moderately sensitive to the flow rate of the gas, so that it was more convenient to design a series of experiments with a constant flow rate of approximately 40 cc. per minute.

The data in Fig. 2 exemplify the reproducibility of the data obtained in actual catalyst testing. In this expt., the catalyst was contained in the all-glass reactor tube shown in Fig. 1. The catalyst was reduced *in situ* with carefully purified hydrogen; the stopcocks for this are not shown in this schematic drawing. The catalyst was cooled from the reduction temperature of 250° in hydrogen, and then was flushed out with the purified helium carrying gas at the reaction temperature of −69.3°. The data shown in Fig. 2 were then obtained by passing 15 successive slugs of synthesis gas over the catalyst and permanent chromatographic tracings from the Speedomax were obtained. The temperature of the thermostatting cryostat was changed between successive slugs according to a schedule reflected in Fig. 2, where lines connect points taken at the same temperature. The cumulative errors in these data are due not only to the errors in the calibration data, but also to those in reproducing the temperatures and to those in the inherent reproducibility of the catalyst. When this is taken into account, the data shown are gratifying.

If points are picked off the curves shown in Fig. 2 at any given slug number and plotted against the reciprocals of the absolute temperatures, a conventional activation energy curve is obtained. Figure 3 was constructed in this manner from the data for the twelfth slug.

In the course of the experimental work[2] over an entire series of catalysts similar to that outlined above, some additional advantages were discovered. These are listed separately below.

(1) When this technique was employed, the glass reaction vessels became nearly isothermal reactors. With the 8-cc. slugs which were passed over the catalyst, even at complete conversion no more than two calories of heat could be liberated. In attempts at steady-state reaction, it was found that at even moderate conversions it was difficult to control the reaction, but in these same tubes, using the microcatalytic technique, there was no evidence of local overheating of the catalyst.

(2) Semi-quantitative estimates of the results obtained by passing a single slug over the catalyst could be made before the next slug was sent over the catalyst. Experimentally this was found to be a great advantage because in a single experiment the information obtained on the first slug could be used immediately to establish conditions for the second, and so on.

(3) The technique was found useful for determining the effects of small amounts of poisons. In this case, data such as shown in Fig. 2 would not be independent of slug number but would constitute a family of curves, falling with slug number.

(4) Similarly, the technique was quite useful, for studies involving changes in activity occurring as catalysts are lined out (brought into a steady state).

(5) With obvious modifications, the same equipment could be used to study steady-state reaction

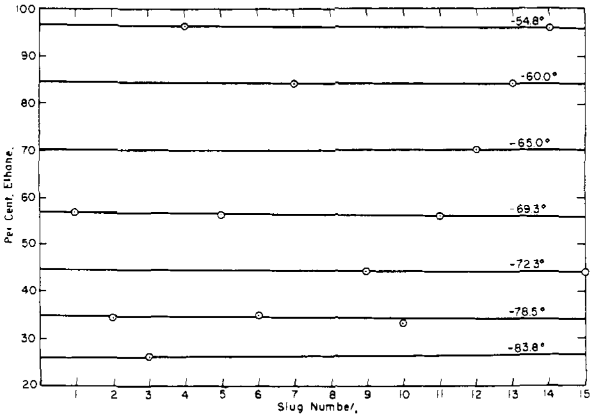

Fig. 2.—Testing data for catalyst IX.

conditions. In this case, a stream of synthesis gas would be passed over the catalyst and the doser would be used to collect measured volumes of the tail gas. This in turn would be carried through the chromatographic column as before, so that most of the advantages listed above would be applicable.

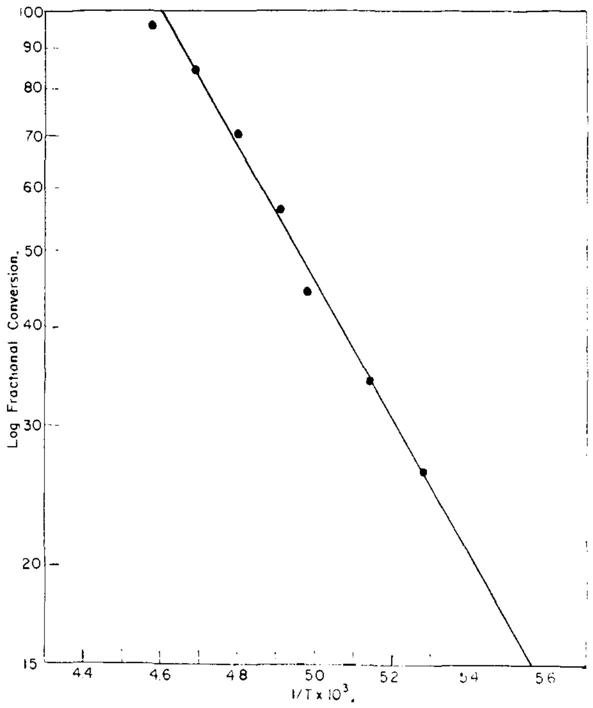

Fig. 3.—Activation energy data picked from Fig. 2 at the twelfth slug.

(6) In the present work, adsorption chromatography[3–6] was used because it was most convenient in dealing with the low molecular weight gases of interest. Vapor phase chromatography[5–11] would be preferable for studies involving molecules of higher molecular weight.

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Capacity of the Electrical Double Layer between Mercury and Aqueous Sodium Fluoride. II. Effect of Temperature and Concentration

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The differential capacity of the electrical double layer between mercury and aqueous solutions of sodium fluoride has been measured at five different temperatures and four different concentrations. The results are in agreement with a theory previously proposed. The results also provide several clues to the anomalous behavior of the electrical double layer and suggest a new theory according to which the rise in the capacity on the *anodic* side of the potential of the electrocapillary maximum is attributed to electrostriction. The "hump" is attributed to the formation of a pseudo-crystalline semi-rigid layer through which anions pass only with difficulty, but without activation energy. The solvent next to the metal never achieves a state of free rotation comparable to that which it enjoys in the bulk of the liquid, which is offered as a partial explanation for the fact that the dielectric coefficient of the substance making up the inner layer is so much lower than that of pure water.

Introduction

The fluoride ion is unique among the univalent anions so far investigated in that it exhibits little or no specific adsorption on mercury even when the latter is positively charged.[1–3] This makes it particularly useful as a tool for studying the properties of the electrical double layer on mercury, since it eliminates the most complicating factor.

The choice of a positive ion is dictated largely by convenience, since monatomic cations are never observed to be chemisorbed on mercury. The sodium ion has several advantages for this investigation as follows: (1) its mobility in water is nearly the same as that of the fluoride ion,[4] which tends to reduce or eliminate liquid junction potentials between two concentrations of aqueous sodium fluoride, or between sodium fluoride and potassium chloride in solution. (2) Unlike KF and NH_4F, so-

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