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Study of Metal Catalysts by Temperature Programmed Desorption

I. Chemisorption of Ethylene on Silica-Supported Platinum*

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An attempt was made to extend the temperature programmed desorption (TPD) technique to the study of metal catalysts by investigating the chemisorption and surface reactions of ethylene on silica-supported platinum. Self-hydrogenation was observed at room temperature as an important part of the process. In addition, a large fraction of ethylene remained irreversibly adsorbed, undergoing farther self-hydrogenation at about 100° and decomposition to methane at around 220° as the temperature was raised during the subsequent TPD. A second decomposition, observed at temperatures higher than 500°, is probably due to the formation of methane from the fragmental surface residue left after the first (lower temperature) decomposition. The temperature programmed desorption technique was applied in this instance not only to the simple desorption processes but also to the surface reactions which give desorbed material different from the initially chemisorbed species.

INTRODUCTION

Temperature programmed desorption technique has proved useful in the study of chemisorption and surface reactions on oxide catalysts (*1*). For metal catalysts, on the other hand, this technique has not been used so far although the related flash filament desorption technique has been extensively used by many investigators. The flash filament desorption is a very sensitive and useful method for clean metal surfaces but its application is limited to filaments and depends on the use of special experimental conditions since it usually requires ultrahigh vacuums. The temperature programmed desorption technique, though not as sensitive as the flash filament desorption, is easier to maintain and operate, and can be, in principle, applied also to conventional catalytic materials. When combined with other techniques employed in catalyst studies, it may be expected to help in the characterization of the surface properties of catalysts.

In the present work an attempt was made to extend the temperature programmed desorption technique to a practical metal catalyst. The main difficulty in extending the technique to metals as opposed to oxide catalysts is the usually much smaller surface area of metal catalysts. Silica-supported platinum was chosen because it provides a sufficient surface area while the support itself (Cab-o-sil) proved to be inert towards the gases used for chemisorption on the metal. The main emphasis was placed on the chemisorption and surface reactions of ethylene. In previous work (*2–5*), self-hydrogenation of olefins was observed on metal catalysts

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even at relatively low temperatures. The self-hydrogenation of ethylene on nickel was recently extensively studied by McKee (6) and by Hirota and Teratani (7). Much less information, however, is available on the corresponding process on platinum. It was therefore thought that it might be of interest to study the behavior of ethylene on platinum using the temperature programmed desorption technique. As part of the same study, experiments were also carried out with hydrogen and carbon monoxide.

EXPERIMENTAL METHODS

Apparatus. The apparatus used for the present study was essentially the same as described before (8), except that pressures were measured with a Pirani gauge instead of mercury manometers in order to prevent catalyst contamination by mercury vapour. A mercury manometer and a McLeod gauge were used occasionally to calibrate the Pirani gauge, but were then isolated from the reaction system by means of a stopcock.

Materials. The silica-supported platinum catalyst was prepared by mixing Cab-o-sil M-5 with a chloroplatinic acid solution. The mixture was dried in an oven overnight at 120°, broken into pieces (about 1 mm^3), and loaded in the reactor. The amount of the catalyst taken was 0.35 g and analysis showed a platinum content of 4.6 wt %. A silica gel catalyst was also prepared for comparison from the same batch of Cab-o-sil by mixing it with hydrochloric acid solution which had the same chlorine ion concentration as the chloroplatinic acid solution used for the platinum on silica catalyst.

Ethylene was taken from a Phillips research grade cylinder and degassed repeatedly in a liquid nitrogen trap. Matheson's ultrahigh purity hydrogen (99.999%) was passed through a liquid nitrogen trap and used without further purification. Cylinder helium was used as carrier gas in TPD after passing through a purification train (molecular seive at room temperature, platinum on asbestos at —195°, and glass beads at —195°).

Procedure. The catalyst was first reduced in a stream of hydrogen for 8 hr at 350°. In the final stage of each run, however, the catalyst was heated up to 650° in the stream of carrier gas, as mentioned below. Evacuation and cooling were then started simultaneously. When the temperature reached 400°, hydrogen was admitted at a pressure of 250 torr, and the catalyst was left overnight at room temperature with the hydrogen present. It was again heated at 400° and evacuated for 1 hr, followed by cooling *in vacuo* to the reaction temperature for the next run. The catalytic activity fell at first, but became reasonably stable after about 30 runs. All data reported here were obtained with the stabilized catalyst. The BET surface area measured with nitrogen after the stabilization was 160 m^2/g.

In a typical experiment with ethylene, a known amount of ethylene was admitted in the reaction system, and collected again after the reaction (chemisorption) by evacuating the system through a liquid nitrogen trap. The reaction time was 20 min, and evacuation was carried out for 15 min at the reaction temperature. The amount of gas collected was measured manometrically and then analyzed by a gas chromatograph with a 2-m alumina column at room temperature.

The material still remaining on the catalyst after evacuation was removed by the temperature programmed desorption: the helium carrier gas was diverted to flow through the reactor and the catalyst temperature was increased at a constant speed of about 15°/min. The gases desorbed by heating into the carrier gas stream were continuously monitored with a thermistor thermal conductivity detector and a recorder tracing (a "chromatogram") was obtained. A more detailed description of the temperature programmed desorption method has been given elsewhere (1). The heating was stopped at about 650°, and the catalyst was evacuated while it was allowed to cool to 400°. Hydrogen was then admitted into the reactor as described before.

Adsorption of hydrogen, carbon monoxide, and ethylene on Cab-o-sil without platinum was also measured in separate experiments. The adsorption of hydrogen and carbon monoxide was negligible, at least at room temperature. Ethylene adsorption was much larger than of the other two gases, but it was still about 10 times smaller than on the platinum on silica catalyst under the same conditions. Moreover, ethylene adsorbed on Cab-o-sil could be removed almost completely by pumping at room temperature, and no chemical reaction occurred. Therefore the effect of silica support was ignored in the present study.

Results and Discussion

Chemisorption of Hydrogen and Carbon Monoxide

The adsorption isotherms of hydrogen and carbon monoixde on the Pt–SiO_2 catalyst were measured in the conventional way. Both adsorptions occurred very quickly. Curve A in Fig. 1a shows the adsorption isotherm of hydrogen at 25° on the catalyst evacuated for 75 min at 600°. After these measurements, the catalyst was evacuated for 2.5 hr at —60°, and a new isotherm shown by curve B in Fig. 1a was determined at 25°. Analogous experiments were also carried out with carbon monoxide and the results are shown in Fig. 1b. As shown in Fig. 1b, increase in the evacuation time at —60° from 30 to 60 min did not affect isotherm B, i.e., the weakly adsorbed (physisorbed) CO was adequately removed in 30 min.

Both with H_2 and CO the broken lines representing the difference A — B tend to constant values at pressures of these two gases in excess of about 20 torr. Assuming that the limiting pressure independent value of A — B for H_2 (0.63 ml/g or 0.22 ml for the actual quantity of the catalyst used) corresponds to saturation of the platinum surface and that H_2 is adsorbed dissociatively, the atomic ratio of H/Pt is found to be 0.24, which seems reasonable for an impregnated platinum-silica catalyst (*9*). Assuming further that the cross sectional area of a Pt atom is roughly $9\ \text{Å}^2$, the surface area of the exposed metal, calculated from the saturated amount of hydrogen, is about $1\ m^2$ for the actual amount of catalyst used (0.35 g).

The number of CO molecules corresponding to the saturation of the metal surface is apparently smaller than that of H atoms (0.25 ml versus 2 × 0.22 ml), and the ratio of H/CO is 1.76, as calculated from the limiting A — B values in Fig. 1. Dorling and Moss recently discussed the configurations of CO molecules on platinum

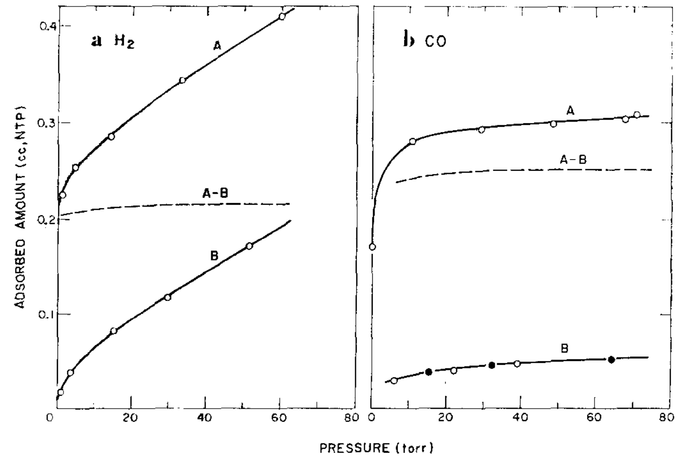

FIG. 1. Adsorption isotherms on Pt-silica catalyst at room temperature: catalyst wt, 0.35 g. (a) H_2: A, adsorption isotherm on bare surface; B, adsorption isotherm taken after evacuation for 2.5 hr at −60° after A. (b) CO: A, adsorption isotherm on bare surface; B, adsorption isotherm taken after evacuation at −60° for 30 min (○) and 60 min (●) after A.

surfaces, and they found that the ratio of (total Pt atoms exposed)/(number of CO molecules adsorbed) on Pt on silica catalysts varied from 1 to 2 depending on the concentration of platinum (*10*).

The temperature programmed desorption of H_2 from the silica-supported platinum at a constant rate of temperature increase of 15°/min gave a reasonably sharp peak which appeared between 100 and 300° depending on the amount of the gas on the catalyst. The TPD of CO, on the other hand, gave a very flat and broad chromatogram, beginning at about 50° and extending up to about 600°. The reason for the unusual behavior of CO has not been established, although it may perhaps be related to a surface interconversion of the two forms (linear and bridged) of adsorbed CO during its thermal desorption. Additional experimental work will be required before a more detailed discussion of the TPD chromatogram of CO may become possible.

Chemisorption and Surface Reactions of Ethylene

The adsorption of ethylene on the silica-supported platinum catalyst also occurred very rapidly. When the amount of ethylene admitted into the reactor at room temperature was small, all ethylene was adsorbed irreversibly and the gas-phase pressure remained smaller than 10^{-3} torr. During subsequent evacuation through the liquid nitrogen trap, 20 min after ethylene was admitted into the reactor, no ethylene or any products were recovered. When the amount of ethylene admitted became larger than 0.035 ml, however, ethane was found in the trap, and the amount of ethane formed increased linearly with the adsorbed amount, as shown in Fig. 2. As mentioned in the preceding section, a monolayer of H_2 on this catalyst corresponded to 0.22 ml for the actual amount of catalyst. The minimum amount of ethylene required to produce ethane (0.035 ml) corresponded, therefore, to 16% of this monolayer of hydrogen. The gas phase pressure still remained 10^{-3} torr or less and only ethane was found in the trap during the evacuation after the reaction as long as the amount of ethylene admitted into the reactor did not exceed 0.07 ml, which corresponded to 32% of the monolayer of hydrogen.

In an experiment with C_2D_4 after the same treatment of the catalyst (treatment with H_2 at 400° followed by 1 hr evacuation at 400°), it was found that the ethane formed was entirely C_2D_6 within the likely uncertainty in the correction for the C_2D_3H impurity in C_2D_4. It is clear, therefore, that the ethane formed and recovered at room temperature resulted from self-hydrogenation of ethylene and not from an interaction with hydrogen which might have remained on the catalyst after its preetreatment with hydrogen at 400°.

The behavior observed in this work with the silica-supported platinum agrees well with the results reported in the literature for ethylene on nickel (*2*, *4*, *6*, *7*), palladium (*5*), and tungsten (*3*), although the minimum surface coverage required for the self-hydrogenation to become appreciable is somewhat smaller on platinum (16% of

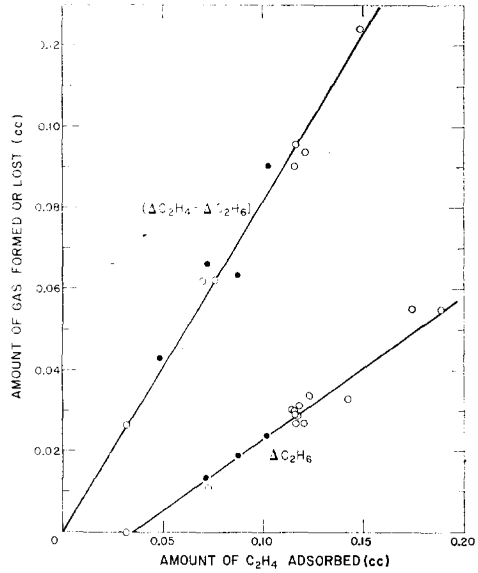

FIG. 2. Amount of gases reacted as a function of the adsorbed amount of ethylene: catalyst wt, 0.35 g; ΔC_2H_6, the amount of ethane formed and trapped at room temperature; (ΔC_2H_4 − ΔC_2H_6), the amount of ethylene lost in processes other than ethane formation during adsorption and TPD; (●), the results with preadsorbed CO.

a hydrogen monolayer) than usually found on other metals (about 25%).

Figure 2 also includes the plot of the loss of ethylene in processes other than ethane formation during the adsorption and the subsequent temperature programmed desorption. This is discussed below, together with the effect of CO poisoning.

Poisoning by CO

Figure 3 shows the results of experiments in which carbon monoxide was preadsorbed on the catalyst before ethylene was admitted. The amounts of CO used were so small that its gas phase pressure was negligible and the reactor was therefore not evacuated before the subsequent admission of ethylene. Ethylene was admitted to an approximately constant pressure of 4 torr. The amounts of ethane formed during the adsorption and of ethylene lost in processes other than ethane formation during the adsorption and TPD both decrease in a linear manner as the amount of CO preadsorbed on the catalyst is increased. It appears therefore that preadsorption of CO on the catalyst merely reduces the number of sites available for the chemisorption of ethylene.

Extrapolation of the lower straight line in Fig. 3 shows that 0.17 ml of CO is needed to inhibit completely the self-hydrogenation of ethylene. This amount corresponds to 68% of a monolayer of CO (0.25 ml), that is at least 32% of the surface must be available so that ethylene chemisorption will result in the formation of some ethane. With unpoisoned catalyst, the minimum surface coverage of ethylene required to form ethane is 16% (on a mole to mole basis) of the hydrogen monolayer, as already pointed out, and this also corresponds to 32% of the surface if ethylene is adsorbed dissociatively as

$$C_2H_4 \rightarrow \underset{*\ *}{C_2H_2} + \underset{*}{2H}.$$

The agreement suggests that ethylene molecules must be adsorbed in close proximity to each other for the self-hydrogenation to take place, and if CO covers (randomly) more than 68% of the platinum surface, the surface species subsequently adsorbed are too far apart to react.

It is also of interest that the results with preadsorbed CO in Fig. 2 do not deviate from the linear plots, although much larger pressures of ethylene had to be used in these experiments than with the unpoisoned catalyst surface to obtain the same adsorbed amount. This indicates that the reactions responsible both for the self-hydrogenation and for the loss of ethylene in other processes take place among the adsorbed molecules and do not involve the gas phase molecules directly.

The rate of consumption of ethylene in processes other than ethane formation is directly proportional to the adsorbed amount of ethylene and goes through the origin (Fig. 2). It would appear therefore that the reaction probably does not require the presence of a neighboring molecule. This is also supported by the fact that more

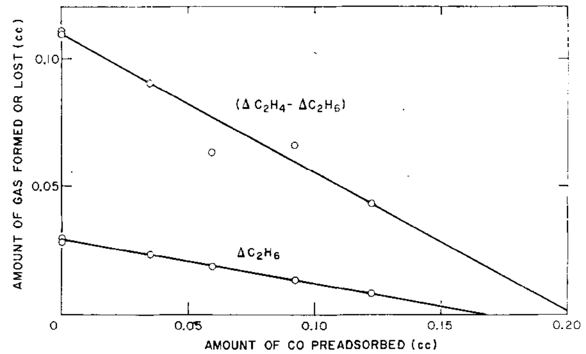

FIG. 3. The effect of preadsorbed CO: catalyst wt 0.35 g; ΔC_2H_6 and (ΔC_2H_4 − ΔC_2H_6), as given in Fig. 3 legend.

CO is needed to inhibit this reaction than for self-hydrogenation, as seen in Fig. 3.

Temperature Programmed Desorption

The solid line in Fig. 4a is a typical temperature programmed desorption chromatogram obtained after chemisorption of ethylene on the silica-supported platinum catalyst, that is, ethylene was adsorbed for 20 min at room temperature and then evacuated for 15 min at the same temperature before TPD was carried out. The broken line in Fig. 4 is the TPD chromatogram taken under the same conditions but with a liquid nitrogen trap inserted between the reactor and the detector, so that only noncondensable gases were detected. Figure 4a shows that the first peak, at about 100°, is that of a condensable material and gas chromatographic analysis showed it to be ethane with a trace of ethylene. The second peak appears at about 220° and should be either methane or hydrogen or both. Finally a peak corresponding to a noncondensable material appeared once again at very high temperature (600–650°).

Using ethane instead of ethylene, but under similar conditions of preadsorption and evacuation before TPD, chromatograms shown in Fig. 4b were obtained. The first "condensable" peak, at 80–90°, was exclusively ethane. As in the case of ethylene, the second peak was "noncondensable," but this time it apeared at much lower temperature (160–170°). Another "noncondensable" peak appeared again at high temperature.

It is not very clear at this stage whether the ethane peak (first peak) in Fig. 4a appeared as a result of self-hydrogenation which occurred at elevated temperatures during TPD or simply represented desorption of ethane which was formed at

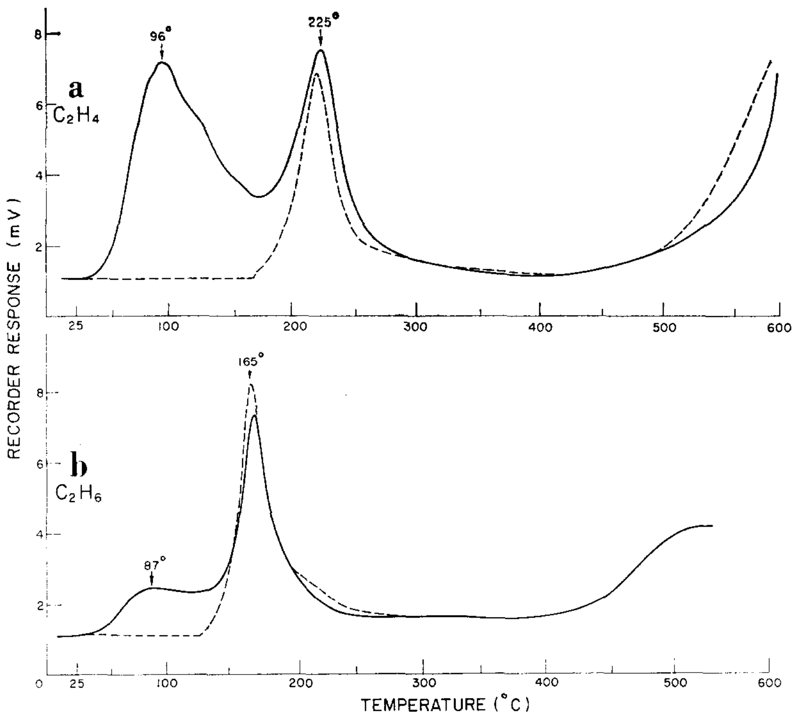

FIG. 4. TPD chromatograms: (a) TPD chromatogram of C_2H_4. Preadsorbed amount, 0.085 ml; total C_2 hydrocarbons remaining on the surface before TPD, 0.074 ml; C_2H_6 desorbed in the first peak, 0.023 ml. (b) TPD chromatogram of C_2H_6: preadsorbed amount, 0.054 ml; total C_2 remaining before TPD, 0.024 ml; C_2H_6 desorbed in the first peak 0.009 ml; heating rate 15°/min; – – –, obtained with a liquid nitrogen trap inserted between the reactor and the detector.

room temperature but remained on the surface during and after the evacuation preceding TPD. It is believed, however, that the former mechanism is more likely, because the amount of ethane desorbed in Fig. 4a is much larger than in 4b, in which a greater amount of ethane was originally adsorbed than was desorbed in 4a, yet most of it was removed by evacuation. The amount of ethylene remaining on the surface becomes, of course, smaller as self-hydrogenation proceeds during TPD. McKee (*6*) found on nickel, however, that the minimum adsorbed amount of ethylene required to form ethane became also smaller as the temperature was increased.

Although the first "noncondensable" peak (the second peak) in Fig. 4a was not analyzed, it is probably mainly methane since the only other possibility, hydrogen, has a very small thermal conductivity response in the helium carrier gas and would give a negative peak. McKee (*6*) found that methane was the sole product in the gas phase when ethylene was contacted with nickel at 200°. He also observed in a static system that ethane formation by the self-hydrogenation of ethylene on nickel reached a maximum at about 150°, but the formation of methane started at about 60° and increased rapidly at 200–210°. On the other hand, in the case of ethane, he found that the formation of methane reached a maximum at 150°, i.e., at a temperature much lower than in the case of ethylene. These observations with methane are in good agreement with the peak temperatures shown in Fig. 4, although the metals used in the two studies were different and Fig. 4 was obtained by a dynamic method.

The first "noncondensable" peak in the ethylene chromatogram seems to be due to the decomposition either of strongly adsorbed ethylene or of acetylenic residue. The calculated hydrogen:carbon atomic ratio in the surface residue after the first peak (ethane) was removed, was 1.4–1.7. The different peak temperature in the ethane chromatogram suggests a different process, possibly the decomposition of adsorbed ethyl radicals.

The process involved in the second "noncondensable" peak (the third peak, at high temperature) is not yet known. It is possible, however, that this peak represents the formation of methane from the adsorbed methyl, methylene, or methylidyne radicals deposited on the surface in the course of the decomposition occurring in the second peak.

The Activation Energies

The temperature (T_M) corresponding to the maximum of a TPD peak is independent of the amount of the sample on the surface if the surface sites are energetically homogeneous and the desorption takes place irreversibly without the back reaction occurring. A simplified mathematical treatment is applicable to this idealized case. If the sites are not of uniform energy or the rate of readsorption cannot be neglected, however, the value of T_M changes with the surface coverage, generally becoming larger as the coverage is decreased (*1*). In the present study, therefore, the peak temperatures (T_M) of the first and second peak in Fig. 4a were carefully checked by varying the amount of gas remaining on the surface and they did not vary within the experimental error.

The two peaks in the ethylene chromatogram, however, are not simple desorption peaks, but correspond to surface reactions. That is, the self-hydrogenation of ethylene and the decomposition of the surface residue are the rate-determining steps for the appearance of the two peaks, giving, respectively, ethane and methane. The constancy of the peak temperatures also indicates in this case that the processes are first order. Indeed the amount of ethane desorbed in the first peak increased linearly with the amount of C_2 hydrocarbons remaining on the surface before TPD.

A simplified mathematical treatment is, therefore, applicable to the present case too. The rate of desorption r_d, i.e., the rate of decrease of the surface reactant, is proportional to the surface coverage of the reactant (θ):

$$r_d = -v_m\, d\theta/dt = k_0\theta \exp(-E/RT), \quad (1)$$

where v_m is the monolayer amount of the reactant but E is the activation energy of the surface reaction instead of the activation energy of desorption in the simple desorption case. The form of Eq. (1) is the same as for the ideal desorption from homogeneous surfaces (*1*, *11*), so that the following equation is valid for linear temperature programming:

$$2 \log T_M - \log \beta = E/2.303RT_M + \log Ev_m/Rk_0, \qquad (2)$$

where T_M is the peak temperature and β is the speed of temperature increase, i.e., $T = T_0 + \beta t$.

Figure 5 shows the plot of the left hand side of Eq. (2) against $1/T_M$ by varying β over a wide range. Both for the first (self-hydrogenation) and the second (decomposition) peak reasonably good linear plots are obtained, giving for the rate constants (k_0/v_m) $4.65 \times 10^4 \exp(11.1 \times 10^3/RT)$ sec^{-1} and $1.75 \times 10^{15} \exp(37.3 \times 10^3/RT)$ sec^{-1}, respectively. It should be noted that the above activation energies refer to the energy states of adsorbed species and not to gas-phase molecules.

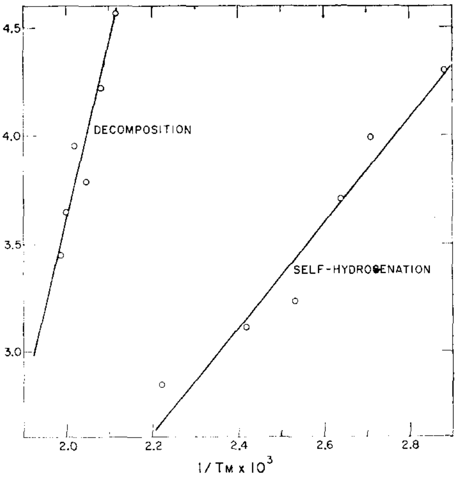

FIG. 5. Plot of Eq. (2): β was varied from 6 to 280°/min for the self-hydrogenation peak and from 6 to 160°/min for the decomposition peak.

Unfortunately, no activation energy values appear to be available in the literature for direct comparison. McKee (*6*) obtained 3 kcal as an apparent activation energy of ethylene self-hydrogenation on nickel, and he assumed that the rate-controlling step was the combination of chemisorbed hydrogen atoms and gaseous ethylene molecules. However, this is not likely to be the case in the present study, because the gas-phase pressure of ethylene did not affect the formation of ethane, as already pointed out.

CONCLUSIONS

The primary motivation for the present study was to extend the temperature programmed desorption technique to a metal catalyst, with a relatively very small surface area of the exposed metal. It is evident that such an extension is feasible and that the technique is capable of providing useful information. Although further work will be required towards a fuller understanding of the behavior of olefins on platinum surfaces, the results obtained give an insight into the behavior of ethylene on silica-supported platinum.

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