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Kinetics of Carbon Formation from Acetylene on Nickel

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The kinetics of the formation of carbon from acetylene on nickel foils at 400–600°C were studied using a microbalance, both in batch and flow conditions. In batch experiments curves of rate of reaction versus conversion show two maxima. The first one was interpreted in terms of a combined effect of nucleation and self-poisoning, while the second maximum could be conveniently explained by an autocatalytic effect of hydrogen. A steady rate of deposition was observed in flow conditions after some time. This offered the basis for the evaluation of the activation energy and of the orders of reaction. The results obtained are in agreement with a previously proposed mechanism.

INTRODUCTION

There has been a great interest in recent years in the study of catalytic carbon deposition on metals. Carbon deposition from acetylene on nickel is perhaps the most studied reaction (*1–10*). However, most studies have covered the morphological aspects of the deposition only (*2–5,10*). Information about the kinetics of the process has been scarce (*6–9*).

Various suggestions have been made as to the mechanism of the process. Presland and Walker (*2*) considered three possible mechanisms, namely, polymerization, surface diffusion and precipitation of dissolved carbon during cooling. An alternative mechanism has been suggested for carbon formation from hydrocarbons on metals in general (*6*). This mechanism was postulated to explain the observed kinetics of the deposition from various hydrocarbons in the range of temperatures 300–600°C. Various types of growth were considered (Fig. 1), but basically, the mechanism assumes that the gas is adsorbed on the metal surface, and carbon atoms are produced by hydrogenolysis and dehydrogenation reactions. The atoms then migrate through the nickel to active growth areas (possibly intermediate carbides) where growth of carbon occurs. Columns can then grow from the metal surface, carbon being supplied from underneath (Fig. 1a). Alternatively, nickel particles can be forced to separate from the bulk nickel during nucleation and can act as centers of carbon growth, originating other types of deposit, including whiskers (Fig. 1b and c). The model explains most of the kinetic features observed and has been discussed in detail (*9*).

A more elaborate version of the proposed mechanism is presented in Fig. 2. The type of Arrhenius plot that might be expected from such a mechanism is also shown. This is discussed below.

Independent work by Baker *et al.* (*10*) using controlled atmosphere electron microscopy has come in support of this mechanism. It is of interest to note here that diffusion of carbon through nickel has also been assumed to explain recrystallization of carbon catalyzed by nickel at ca. 1000°C (*11,12*).

It seemed desirable to have detailed information about the *kinetics* of carbon formation from acetylene on nickel in order

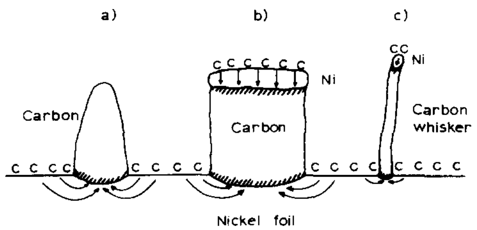

FIG. 1. Various modes of carbon growth.

to complement the information available from studies of the *morphological* aspects. The present study was undertaken with this purpose. In the light of the crossed information from these two types of studies we can best discuss the validity of the proposed model for carbon formation from gases in the present system.

METHODS

Procedure

The present kinetic studies were carried out in a vacuum microbalance system. The system and the technique used have been described in detail elsewhere (*6,7,13*). The sample was cut to a convenient size, weighed, cleaned with chloroform and suspended in the microbalance. In batch experiments the system was then degassed at room temperature to 10^{-2}–10^{-3} Torr and the reactants were admitted up to the working pressure. The weight of carbon deposited was continuously recorded as a function of time. These data were fed to a Hewlett Packard 9820 A computer and alternative plots were obtained.

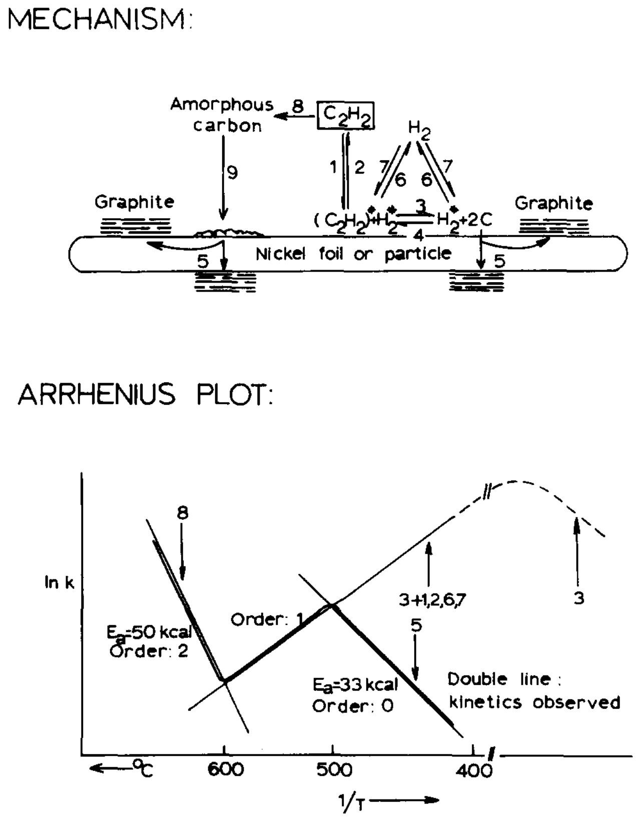

FIG. 2. A more elaborate version of the proposed mechanism, including the following steps: (1) Adsorption of acetylene; (2) desorption of acetylene; (3) surface decomposition; (4) surface reformation; (5) carbon diffusion through nickel; (6) hydrogen desorption; (7) hydrogen adsorption; (8) homogeneous pyrolysis; (9) diffusion to the surface. *The nature of the adsorbed species is not stated.

The orders of reaction at a given temperature were measured in flow conditions. The system was allowed to attain steady state deposition at fixed flows of hydrocarbon, hydrogen and nitrogen and then the flow of one of the components was increased step by step. To obtain activation energies, various series of experiments with changing temperatures were performed both in batch and flow conditions. The temperatures were changed step by step upwards and downwards in each series to make sure that reproducible rates of reaction were being recorded.

Materials

The nickel was used in the form of thin foils (purity 99.7%). The gases (C P grade, 99% purity or better) were supplied by Mogás (acetylene, nitrogen and hydrogen) and Air Products (olefins) and were further purified to remove H_2O and H_2S.

RESULTS

Batch Experiments

It has been previously reported that acetylene forms carbon on nickel more readily than the olefins (*6*,*9*). This is shown more clearly in the series of experiments at 500°C presented in Fig. 3. The deposition from acetylene is faster. In the absence of hydrogen as a reactant the deposition from acetylene is only slightly delayed, while in the case of 1-butene a very long induction period is observed.

The effect of acetylene pressure on the deposition at 500°C is shown in Fig. 4a. The curves present various inflexions, and a representation of the rate of deposition rather than the deposited weight is more informative (Fig. 4b). For brevity, only this representation is used in the results presented next. The curves show two maxima, in general, and the pressure of the hydrocarbon has a positive effect on the height of both of them up to 100 Torr (1 Torr = 133.3 N m^{-2}). For 200 Torr, however, the deposition is rapidly inhibited at this temperature (Fig. 4a).

All of these were experiments lasting several hours. Only when conversion was complete did the deposition stop. Hydrogen is produced in the reaction but the total pressure did not change. This is in agreement with the assumption that the only important reaction taking place is

$$C_2H_2 \rightarrow 2\ C + H_2.$$

Thus the composition of the reactant gas can be known at any stage. For example, in the rate vs conversion curve for 50 Torr

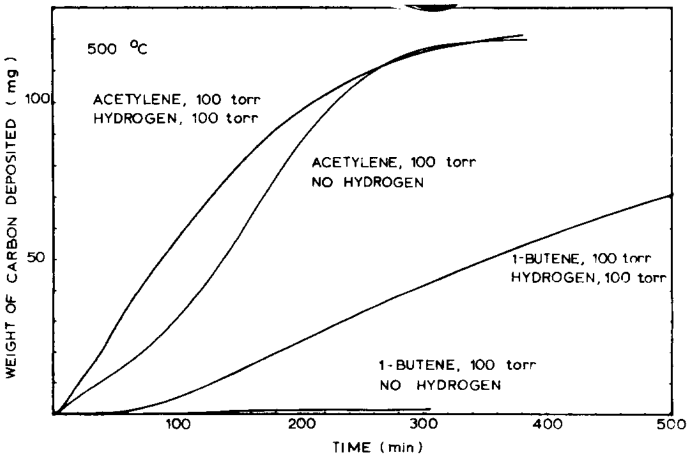

FIG. 3. Carbon deposition from acetylene and from 1-butene on nickel.

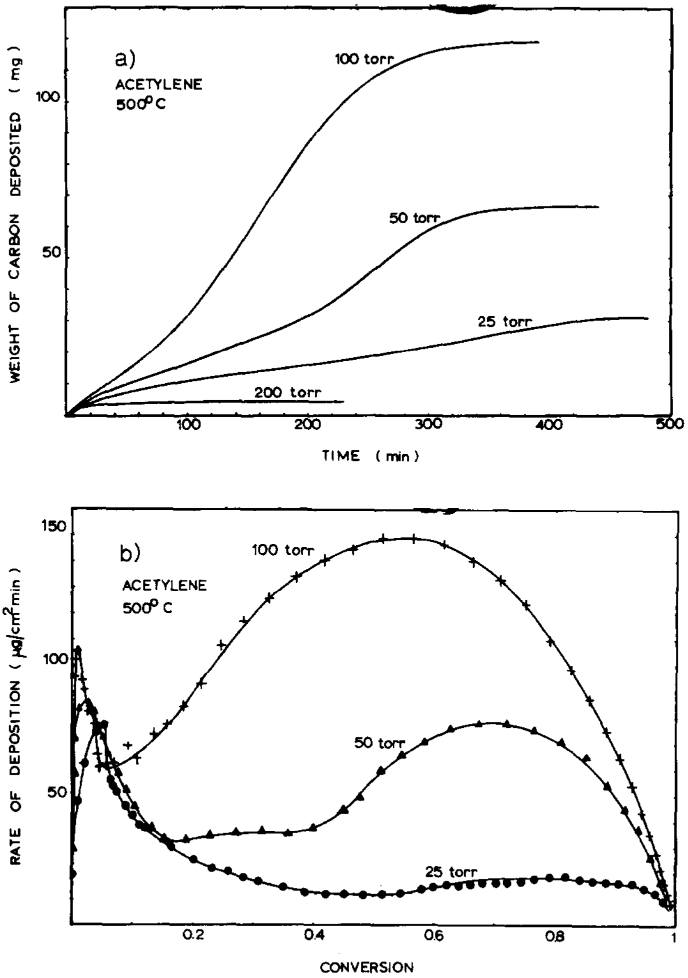

FIG. 4. Carbon deposition from acetylene at 500°C and various pressures (no hydrogen). (a)Weight of carbon deposited vs time of deposition; (b) rate of deposition vs conversion.

shown in Fig. 4b, the composition at the second maximum is 30% acetylene, 70% hydrogen. The partial pressures are 15 and 35 Torr, respectively. So, in the experiments with acetylene only, if the effect of hydrogen is positive, it will be progressively felt in an autocatalytic fashion.

A more direct evaluation of the effect of hydrogen on the reaction was obtained in the series of experiments presented in Fig. 5. As shown, the first maximum increases at higher pressures, but the second maximum decreases and is even nonexistent at 400 Torr.

The occurrence of maxima in the rate of carbon deposition is not new (*5,14*), though it is not observed for carbon formation from olefins on nickel in normal conditions (*15,16*). However, an initial maximum has been observed with olefins in two particular situations. In one case, a carbon-covered nickel foil from a previous experiment was partially scratched and reused (curve A in Fig. 6). In a second case, a 250 µg pre-coating of the foil was made under conditions of slow carbon deposition (*cis*-butene, 50 Torr). The pressure was then increased and a fast accelerating

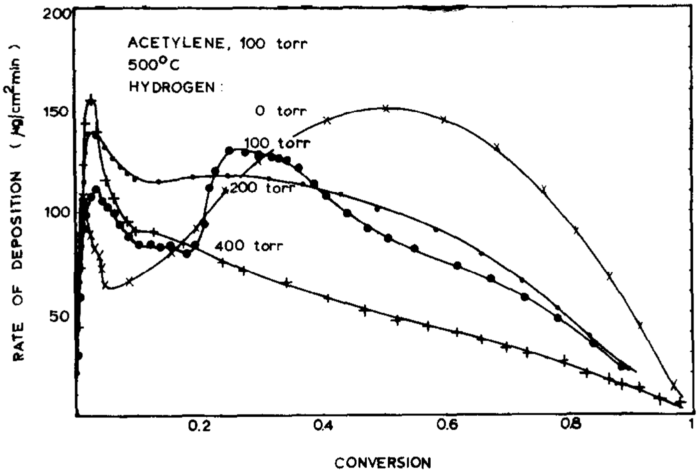

FIG. 5. Rate of deposition vs conversion for 100 Torr acetylene at 500°C and various hydrogen pressures.

rate immediately developed, as usual (curve B in Fig. 6).

Two series of runs were also completed to study the effect of temperature on the reaction. In the first series, only acetylene (100 Torr) was admitted to the system (Fig. 7). Both the first and second maxima increase with temperature up to 525°C. At 550°C the reaction is rapidly inhibited and only a very slow rate of deposition is observed after a few minutes. For the second series of runs regarding the effect of temperature, hydrogen (200 Torr) together with acetylene (100 Torr) were initially admitted to the reactor. The results are presented in Fig. 8a and b. Again, the rate reaches a maximum at about 550°C. Very similar behavior has been reported for carbon deposition from carbon monoxide–hydrogen mixtures on iron (*14*) and acetylene–hydrogen mixtures on nichrome (*5*), and confirms the general pattern observed with unsaturated hydrocarbons on nickel (*7,9*). This common feature, which seems to be found in various catalytic carbon formation processes, is considered when discussing the mechanism.

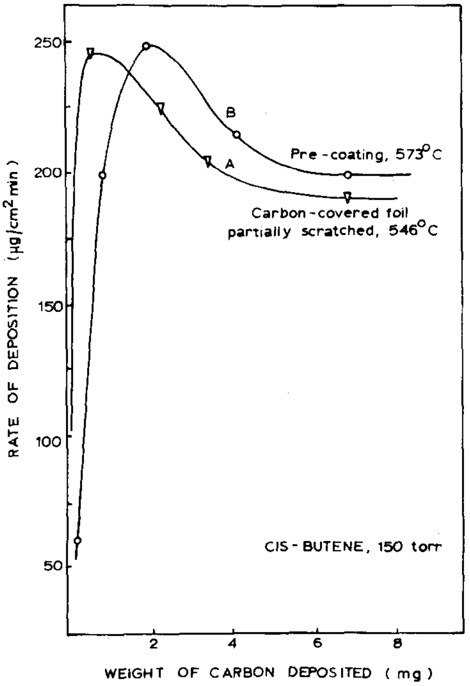

FIG. 6. Maxima in rate of carbon deposition from *cis*-2-butene on nickel.

Flow Experiments

The integral experiments in batch conditions reported above offer a very convenient way of obtaining general information about the main kinetic features of the system (*13*). Some information has been obtained about the influence of time of deposition, temperature and the pressure of hydrocarbon and hydrogen on the rate. However, the crossed effect of the various

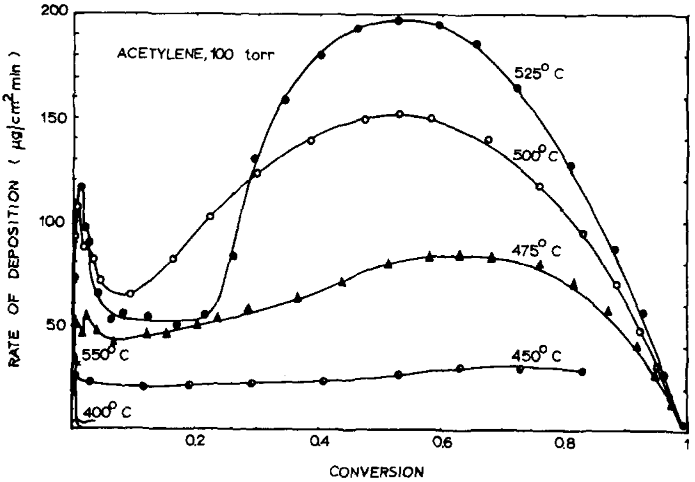

FIG. 7. Rate of deposition vs conversion for 100 Torr acetylene (no hydrogen) at various temperatures.

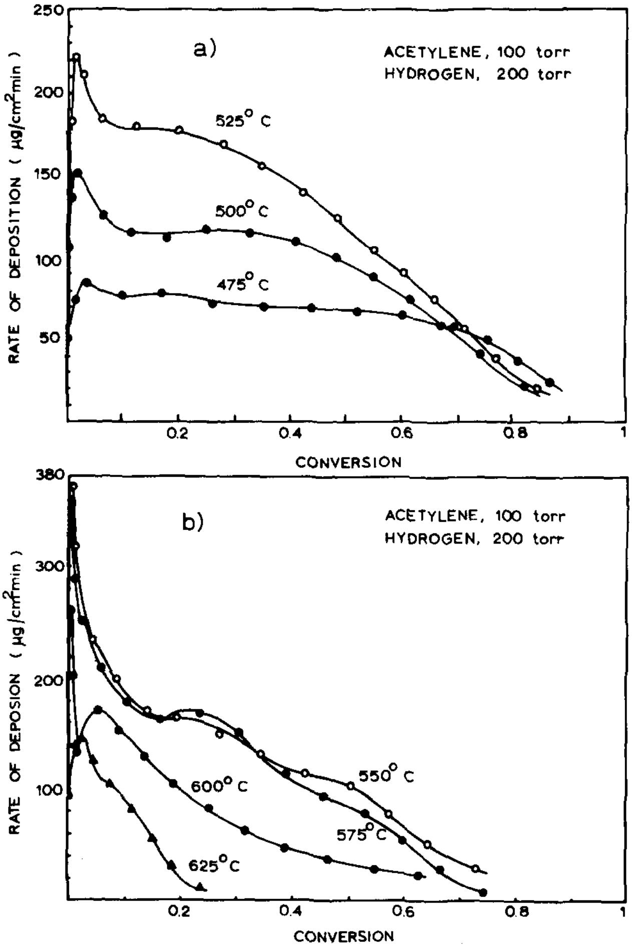

FIG. 8. Rate of deposition vs conversion for 100 Torr acetylene, 200 Torr hydrogen mixtures at various temperatures.

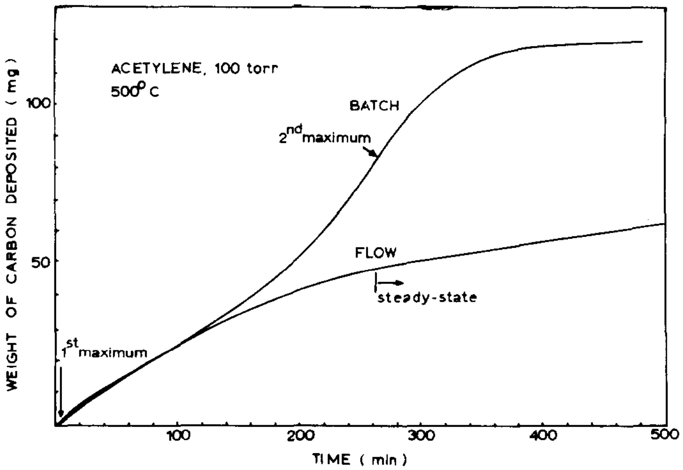

FIG. 9. Carbon deposition from 100 Torr acetylene at 500°C in batch and flow conditions.

variables make it difficult to obtain reliable values of orders of reaction and activation energies from the data presented so far.

Flow experiments present an easy way to obtain differential conditions. If a steady state can be observed after the "development" of the reaction rate, conditions will exist which are particularly favorable for further kinetic studies. This was found to be the case, as shown in Fig. 9. The comparison of the two runs depicted in the figure further shows that the second maximum in rate is due to the effect of hydrogen which accumulates in the system in batch conditions. It is also observed that if the pressure of acetylene is maintained (flow conditions) the reaction does not stop.

Various series of runs were performed to evaluate the activation energy of the reaction in the range of temperatures 400–500°C. These are presented in Table 1. If the hydrogen pressure is low (series A and B in Table 1), a value of about 31 kcal mole^{-1} is obtained, in agreement with

TABLE 1

COMPARISON OF OBSERVED ACTIVATION ENERGIES FOR CARBON DEPOSITION FROM ACETYLENE ON NICKEL UNDER VARIOUS EXPERIMENTAL CONDITIONS

Reference	Activation energies (kcal mole^{-1})	Conditions	Initial pressure (Torr)		Temp range (°C)	Remarks
			C_2H_2	H_2		
A	30.5 ± 1.5[a]	Flow	100	—	415–465	Steady state
B	31.5 ± 1.5[a]	Flow	100	20	405–480	Steady state
C	63.5 ± 1.5	Flow	100	100	420–465	Steady state
D	48.0 ± 2.0	Flow	50	200	405–480	Steady state
E	31.0 ± 1.0[a]	Batch	100	—	405–475	Steady state
F	31.0 ± 1.0	Batch	100	200	450–500	Steady state
G	33.0 ± 1.5	Batch	100	—	400–500	1st max
H	35.5 ± 2.0	Batch	100	—	400–500	2nd max
I	24.5 ± 1.5	Batch	100	200	475–550	1st max
J	20.0 ± 1.0	Batch	100	200	475–525	2nd max

[a] Values which more probably refer to a steady state.

a previously reported value (*7*) and within the range observed for various olefins (*9*). For higher hydrogen pressures, however, very high and disperse values are found (series C and D). This same "anomalous" behavior was noted with ethylene and propylene (*6*,*9*).

It is appropriate to compare the values obtained with the ones that can be calculated using data from batch experiments. If the region of relatively stable rate following the first maximum (see Figs. 7 and 8) is used to change the temperature and evaluate activation energies, the values found are consistent with the ones obtained under flow conditions (series E and F). The validity of estimating activation energies using the rate at the first or second maxima in Figs. 7 and 8 may now be questioned. The values obtained are included in Table 1 (references G to J). It is obvious that the rate under these conditions is not only a function of the temperature but also of the "history," that is to say, of the mode of nucleation and growth. The conclusion is that activation energies based on maximum rates cannot usually have more than an empirical interest. This questions the validity of a value reported elsewhere for this reaction (*10*) taken from data for carbon deposition on nichrome wire (*5*), quoted to show evidence that diffusion of carbon through nickel was the rate controlling step. It is not clear how data of deposition and diffusion on two different metals can be so compared.

A comment must be made regarding the "anomalous" values observed here for the higher hydrogen pressures. Possibly, a change of temperature in this case is accompanied by a change of the morphology, so that a "stable" steady state does not exist.

A maximum in the rate at a temperature (T_{max}) of 500 ± 50°C is observed, as mentioned above, so that a negative apparent activation energy is observed above T_{max}. This was confirmed in four series of runs. The rates observed are shown in the Arrhenius plot presented in Fig. 10. Various conclusions can be drawn from Fig. 10. The order is approximately zero at low temperatures and close to unity above T_{max}. The value of T_{max} increases with acetylene pressure. It can also be concluded, from inspection of Figs. 7 and 8, that T_{max} is further increased with increasing hydrogen pressure.

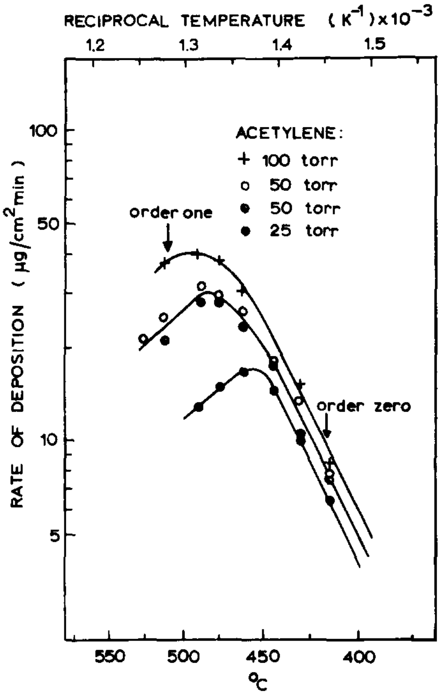

FIG. 10. Arrhenius plots for the deposition of carbon on nickel at various acetylene pressures.

Finally, various series of runs were completed to obtain a direct evaluation of the orders of reaction. The temperatures of 430 and 525°C were selected because they correspond to regions well below and well above T_{max} (cf. Fig. 10), so that the "transition region" was avoided. In fact, orders very close to zero at 430°C and very close to one at 525°C are observed to both acetylene and hydrogen pressure, as listed in Table 2. This is again in agreement with values reported previously for various olefins (*9*).

TABLE 2

Orders with Respect to Hydrogen and Acetylene at Different Temperature in Flow Conditions

Temp (°C)	Pressures (Torr):	25	50	100	200	Remarks
430	Orders to hydrogen	0.4	0.0		−0.3	Acetylene pressure, 50 Torr
525		1.2		← 1.0 →		
430	Orders to acetylene	0.0	0.0		0.2	Hydrogen pressure 30 Torr
525		1.0	1.2		0.6	

DISCUSSION

The curves of rate of deposition vs conversion reported above exhibit in general two maxima. The first maximum may be due to the combined effect of nucleation and self-poisoning, while the second one should be related to the positive effect on the rate of reaction of the hydrogen being produced (autocatalysis). This is discussed next.

The agreement of the kinetics observed with the proposed mechanism is also considered.

Nucleation and Self-Poisoning

The process of carbon formation on a catalytic surface involves: (a) decomposition of the gas on the surface; (b) diffusion of the species formed; (c) growth of carbon.

Before growth can start, nucleation has to take place. If the growth process is the rate controlling step, a continuous acceleration should be observed, as the size and number of nuclei increase. This must be the case in the early stages of the deposition. If the surface reaction were controlling, a continuous decline in rate would be expected, as the area available for the gas reaction is progressively reduced by the growth of carbon on it. Now, when the diffusion step is the slower and controlling one, the rate will be a function of the size and number of both the uncovered metal surface (*source* of carbon atoms) and the nuclei formed (*sink* of carbon atoms). So, an acceleration is to be initially expected, as the nuclei are formed and grow, but at the same time the metal area is being reduced and this will eventually lead to a decline of the observed rate. This is thought to be the cause of the occurrence of the first peak in the rate curves.

If a steady state situation is not reached at some stage, with certain areas being available for the decomposition and other areas being active for growth, the process of self-poisoning may be total and the reaction stops. This is probably what happens in some systems. In the present case, however, a steady state seems to be reached. This is evident from the flow experiments (cf. Fig. 9). Whether a maximum in the rate is observed or not depends on when the steady state is established, early in the acceleratory period or later after some deceleration has already taken place. This could explain the various curves obtained from olefins [cf. Fig. 6 and Ref. (15)] and acetylene.

Autocatalysis

The effect of hydrogen in the reaction is somewhat complex. In Figs. 4b and 5, it is seen that the first peak increases with increasing hydrogen pressure, as it does with acetylene pressure. However, the degree of self-poisoning seems to be also more drastic for higher hydrogen pressures, as observed in Fig. 5. It is interesting to note here that a similarly ambiguous effect of hydrogen addition was reported by Walker *et al.* (*14*) for the carbon deposition from carbon monoxide on iron catalysts.

The effect of hydrogen in the later stages of the deposition is more clear. Assuming that at 10% conversion the process of growth is stabilized, and that the order with respect to acetylene pressure (P_A) and to hydrogen pressure (P_H) are 1, the rate is given by:

$$r = kP_AP_H = kP_{A_0}(1-x)\ (P_{H_0} + P_{A_0}x), \quad (1)$$

where x is the fractional conversion of acetylene and P_{A_0} and P_{H_0} are the initial pressures. This equation expresses the autocatalytic effect of hydrogen on the reaction. Application of Eq. (1) with appropriate k values to the upper and lower runs shown in Fig. 5 (0 and 400 Torr of hydrogen) gives the good fit presented in Fig. 11. The fit for the intermediate curves (100 and 200 Torr) is not good, suggesting that the growth has not stabilized, that is to say, self-poisoning is not confined to the early stages of the deposition. Radical changes in the structure of the deposit possibly go on for a much longer time.

Mechanism

The kinetics under steady state conditions are in general agreement with the proposed mechanism (*9*). Both the orders and activation energies observed have the values that should be expected: orders vary from zero at low temperatures (<475°C) to unity at high temperatures and the activation energy also changes from a positive to an apparently negative value at higher temperatures. This is consistent with a change of rate determining step from carbon diffusion in the metal to a pressure dependent surface reaction (cf. Fig. 2 with Fig. 10 and Tables 1 and 2).

The nonzero orders sometimes observed for hydrogen at low temperatures are somewhat anomalous. In fact, all the evidence points to a carbon diffusion controlled mechanism at these temperatures. The slight effect of hydrogen could possibly be attributed to a rearrangement of the morphology rather than to a purely kinetic effect. An increase in hydrogen pressure may not accelerate the rate of the

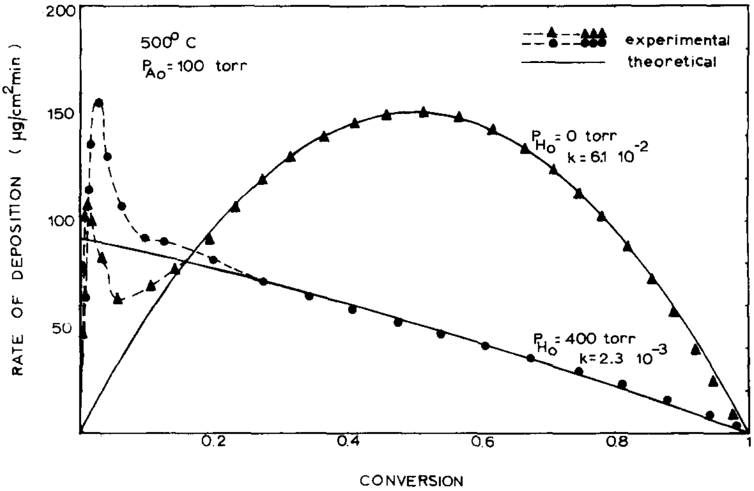

FIG. 11. Experimental carbon deposition rates from acetylene compared to a theoretical autocatalytic model [Eq. (1)].

surface reaction but can have an effect on the stability of the metal particles or other solid phases involved, so that the area available for reaction can be increased or reduced. This is consistent with the somewhat ambiguous effect of hydrogen found in batch experiments (Fig. 5) already discussed.

The rate of growth in the diffusion controlled region of temperatures can be calculated if the exact geometry of the system is known. However, the growth of carbon takes place in various forms in a particular sample, and the increase in weight must be interpreted as a statistical average. Assuming that the area of nickel available for diffusion is of the order of the original metal area, and that it takes place unidimensionally, the average length that the carbon atoms must travel (l) can be calculated. If diffusion through nickel is the controlling step, the rate of growth can be estimated from the equation $Q = D(dc/dx) = D(S/l)$ assuming saturation at the free surface of nickel and virtually zero carbon concentration at the carbon growth side. Values can be calculated for the diffusivity ($D = 1.02 \times 10^{-10}$ cm^2 sec^{-1}) (*18*) and the solubility of carbon ($S = 1.96 \times 10^{-3}$g cm^{-3}) (*17*) at 500°C. These values can explain the observed rates of growth ($Q = 50$ μg min^{-1} cm^2) if l is the order of 2–3 nm (20–30 Å). Although the assumption that the process of diffusion is unidimensional is a rough approximation, the value obtained is certainly of interest as a guide.

A more interesting calculation can be performed if the rate of growth of individual carbon whiskers can be followed. This has been done by Baker *et al.* (*10*). These authors reported that filaments with "pear shaped" particles, 30 nm wide at their ends, grew with a rate of ca. 75 nm sec^{-1} at 600°C. They observed a dense external wall in the filaments and a more loose core, including a central hollow channel. Now, in such a nickel particle, the distance the carbon atoms have to diffuse to feed the wall growth is probably not more than a few nanometers (say, 1-2 nm).

At 600°C we have $D = 3.89 \times 10^{-10}$ cm^2 sec^{-1} and $S = 3.83 \times 10^{-3}$ g cm^{-3}. This gives $Q = 7.5$ μg sec^{-1} cm^{-2}. The linear rate of growth (assuming the density of the carbon to be $\rho = 2$) will be equal to 38 nm sec^{-1}. This is well within the order of magnitude of the linear rate of growth experimentally observed. The diffusion of carbon into the inner regions of the filament is much slower, as the distance to be traveled is of 10 nm or more. So, the growth is 5 or more times slower and the rate at which the core is filled up does not keep pace with the faster wall growth. Accordingly, the density of the core is lower and a hollow channel is seen in the less accessible central region. Also, smaller and thinner particles are expected to give rise to faster linear growth, as observed by Baker *et al.* (*10*). This is in agreement with a diffusion controlled mechanism, as pointed out by these authors.

Now, there is a point which is not clear. If saturation of the nickel is assumed at the surface decomposition side, this increases with temperature [$\Delta H = 9.5$ kcal mole^{-1} (*17*)]. So, the combined effect of an increase in rate with a higher diffusion gradient should be observed in the rate, giving an apparent activation energy of about 43 kcal mole^{-1}. It is not clear whether saturation of the nickel at the source of carbon atoms and virtually zero concentration at the carbon growth areas should be assumed. It is only when a temperature independent concentration gradient in the nickel exists that a value of 33 kcal mole $^{-1}$ for the activation energy of the process must be expected. On the other hand, there is reasonable experimental evidence in favor of diffusion control in the lower region of temperatures.

Various common kinetic features are found in the catalytic process of carbon formation in different systems, like C_2H_2–Ni, CO–Fe (*14*), and others (*5*,*9*).

Two important ones are: (a) occurrence of a maximum rate at a temperature usually in the range 500–600°C, (b) positive effect of hydrogen, especially at the higher temperatures. This suggests that a similar mechanism including diffusion of carbon through the metal is generally operating in catalytic carbon formation processes. This seems to be confirmed by recent work (*19*).

Some progress has been made in our understanding of the process of catalytic carbon formation from gases in recent years. The kinetic method of establishing the mechanism has proved to be of value, particularly when a region of steady growth can be observed.

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