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Carbon Formation from Light Hydrocarbons on Nickel

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Preliminary studies of the formation of carbon from several light hydrocarbons on nickel foils over the temperature range 400–600°C have been completed. Deposition from acetylene was found to be rapid, while deposition from olefins is autocatalytic and is accelerated by hydrogen. Carbon formation from paraffins is comparatively slow.

The mode of pretreatment of the nickel was found to influence the early stages of carbon deposition. Factors such as temperature, pressure of gas, annealing, and order of admission of reagents had a marked effect on the initial rate of deposition. The kinetics of the carbon deposition at later stages of the reaction appear to depend on nickel crystallites transported from the foil surface by the growing carbon.

INTRODUCTION

Although there have been many studies of the kinetics of homogeneous carbon formation and of heterogeneous carbon formation on noncatalytic surfaces, carbon formation on catalytic metal surfaces has been less well studied (*1*). However, iron, cobalt, and nickel have been recognized as active catalysts for carbon deposition, as, for example, in the case of carbon formation from carbon monoxide, both at low temperatures ($<350°C$) where carbides are the final solid products (*2*), and at higher temperatures, where carbon is formed (*3–8*). In spite of the industrial importance of this reaction in the Fischer-Tropsch process, the mechanism is far from being well understood, and conflicting evidence has been presented even in the more recent publications (*5, 6*).

The kinetics of the catalytic carbon formation from hydrocarbons is also of industrial importance. Severe problems of 'fouling' are encountered when the transition metals are used as dehydrogenation catalysts, the reaction requiring thermodynamically the use of high temperatures and low pressures, and no serious attempts to study or to minimize the problem were made since Frey and Huppke (*9*) discovered the superior properties of chromia catalysts in 1933. Recent developments in the use of supported metals in hydrocarbon processing at high temperatures and low pressures (reforming (*10*), steam-reforming (*11*), etc.) has led, however, to a resurgence of interest in the study of catalyst fouling under these conditions. The present paper reports preliminary studies of the kinetics of catalytic carbon formation from various hydrocarbons on nickel.

EXPERIMENTAL

Equipment and Materials

A.C.I. Electronics Mark 1 vacuum microbalance was used for all experiments, in conjunction with a vacuum line operated in the static mode. The sample was suspended from the balance arm so that it was maintained in a constant temperature, controlled atmosphere environment. The temperature was controlled to within ±0.5°C by an A.E.I. RT 3R proportional controller. The output signal of the micro-

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balance was recorded as a function of time: an automatic electronic range switch was incorporated in the circuit, so that the five ranges of the balance could be used in succession during the course of a given experiment, combining maximum sensitivity at early stages with a wide range.

It was possible to analyze both inlet and outlet gases with the aid of an on-line Pye Panchromatograph fitted with a Sevomex microkatharometer.

The hydrocarbons used were supplied by B.O.C. or by the Matheson Company, and were C.P. grade (99%) or better. The purity of the reagent was checked by gas chromatography. Hydrogen and nitrogen were obtained from cylinders (B.O.C., >99.9% purity). The nickel foils were from Metals Research Ltd., purity 2N7 and thickness 0.1 mm.

Procedure

For carbon deposition experiments, a nickel foil was cut to a convenient size and its weight adjusted (on an analytical balance) to a pre-fixed value corresponding to a total area of 3.49 ± 0.01 cm^2. The sample was hung from the balance and first degassed at room temperature (½–1 hr) and then at the reaction temperature (1–2 hr). In many cases, the foil was also reduced by heating at 320°C under 50 Torr of hydrogen before degassing was completed. The hydrocarbon was then admitted to the system and the change in weight due to carbon formation was recorded continuously. Hydrogen could also be admitted as a second reactant by means of a Toepler pump, and the hydrocarbon pressure could be increased in the same way.

The composition of gas mixtures and products was checked by G.L.C. The solid sample was subjected to elemental carbon and hydrogen analysis, to emission spectroscopy, to X-ray analysis, and to electron beam methods. In addition, the surface areas of the final samples could be measured on a standard volumetric B.E.T. apparatus.

RESULTS

Kinetic Features

The formation of carbon on nickel was found to be important at temperatures greater than ca. 350°C. Above ca. 575°C, carbon was also formed in the gas phase and on the silica reactor surfaces: as a result, the catalytic effect of nickel on carbon deposition was investigated between 350 and 575°C.

The formation was found to be autocatalytic with olefins (ethylene, propylene, 1-butene, cis-2-butene, 1,3-butadiene) giving eventually a fast rate of deposition. The course of typical reactions is shown in Fig. 1 for deposition from cis-2-butene as a function of time at various pressures of gas. Three periods can be defined: an induction period, during which there is virtually no formation of carbon; an acceleratory period; and finally a steady state period, during which the rate of deposition is constant. The induction period was particularly long at low pressures and/or temperatures, but was shortened if hydrogen was also present. The final rate of deposition could be as high as 200 $\mu g/cm^2/min$ in the absence of added hydrogen, the rate tending to increase if hydrogen was admitted together with the hydrocarbon.

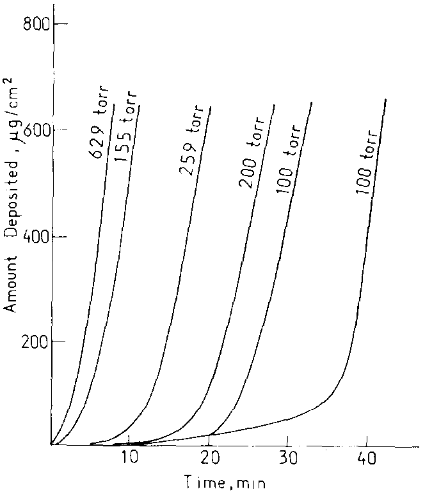

FIG. 1. The amount of carbon deposited as a function of time and pressure. cis-2-Butene, pressure as stated; temperature, 545°C.

Experiments were also completed with paraffins (methane, ethane, propane), but the very slow deposition observed showed no autocatalytic behavior and the rates observed never exceeded 2 μg/cm²/min. Deposition from acetylene, on the other hand, was very rapid and was not affected by the presence of hydrogen.

Analysis of the gas after reaction showed hydrogen as the only detectable product from all reagents (the limit of detection of hydrocarbons was 0.1 Torr).

The effect of various parameters on the course of reaction was examined using olefinic reagents. The length of the induction period was found to be very dependent on the pretreatment of the foil, but the steady state rate was independent of the foil history (Fig. 2, Table 1). The reaction accelerated quickly when the sample was degassed for a long period at reaction temperatures (1 hr or more) or when the sample was not prereduced. Prereduction, followed by degassing at room temperatures led to a long induction period. For equivalent preconditioning, the length of the induction period increased with decreasing temperature, and an Arrhenius plot of the length of the induction period gave a slope equivalent to an activation energy of 100 kcal/mole over the range 475–525°C.

TABLE 1
THE INDEPENDENCE OF THE STEADY-STATE RATE[a]

	Pretreatment	Final rate (μg/cm²/min)
Bare Ni	1 hr degassing, 500°C	68
Bare Ni	1 hr degassing, 500°C 1 hr degassing, 25°C	67
Carbon on Ni	Short evacuation, 500°C	66
Carbon on Ni	>3 hr degassing, 500°C	66–72

[a] Conditions: T = 500°C; pressure, (C_2H_4) 50 Torr, (H_2) 50 Torr.

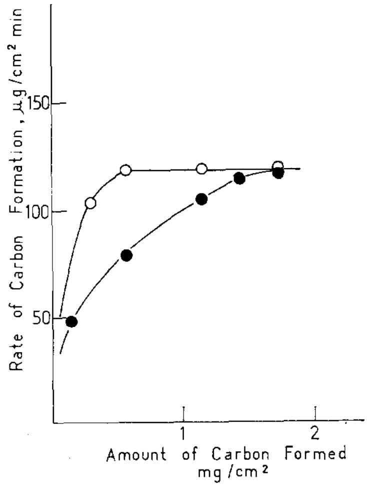

FIG. 2. The independence of the final rate from pretreatment of the foil; cis-2-butene; pressure, 100 Torr; temperature, 545°C. -●-●- Prereduction by hydrogen, followed by degassing at room temperature (1 hr); -○-○- degassing at reaction temperature (1 hr).

The order of admission of hydrogen and olefin was also found to be critical at higher temperatures (ca. 550°C). As shown in Fig. 3, the induction period was considerably longer when hydrogen was admitted prior to the olefin.

The rate of carbon deposition was studied using deposited carbon, shaken clear from the foil, as a catalyst. After a

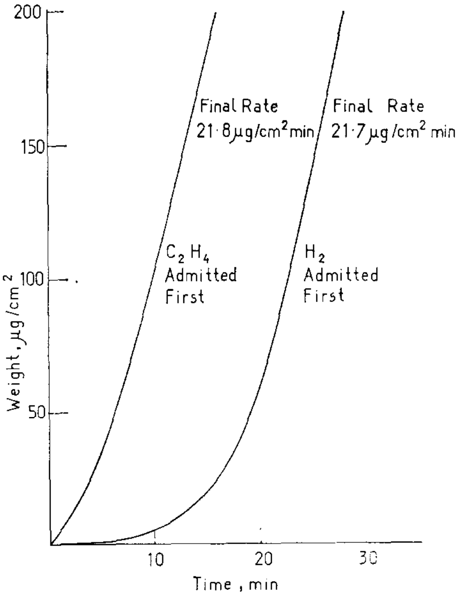

FIG. 3. The effect of order of admission of the reactants on the rates of deposition during the initial stages of reaction.

Ethylene; pressure, (C_2H_4) 25 Torr, (H_2) 25 Torr; temperature, 550°C.

short induction period, the steady state rate observed was very similar to that observed over the original foil + carbon under similar conditions. Pyrolytic carbon, obtained from nonmetallic systems, was inactive.

Properties of the Carbonaceous Deposits

Some investigation of the carbonaceous products has been completed. The carbon was loosely attached to the original metal surface, having a thickness of several millimeters, depending on reaction time. Carbon:hydrogen ratios are given in Table 2, the balance to 100% being attributed to the presence of nickel. This was confirmed by wet chemistry methods and by emission spectroscopy, X-ray analysis, and electron probe studies. From the two latter techniques it was found that the nickel was not atomically dispersed in the carbon, but existed rather as crystallites of the metal, with dimensions of the order of 10–20 μm, suspended in the carbon. The size of these particles was of the same order as the size of the crystallites in the original foil, and decoration of the grain boundaries of the foil by carbon was noted at early stages of the deposition (*12*). The surface area of the carbon separated from the foil was found to be of the order of 110 m^2/g.

DISCUSSION

Investigation of the kinetics of catalytic carbon formation on nickel shows that the ease of carbon deposition increases with the increasing degree of unsaturation of the fuel. Acetylene produces carbon faster than olefins which, in turn, deposit faster than paraffins: in all cases, the products of reaction are the same, no significant distinction (for example, in the C:H ratio) being possible between the products from different reagents.

TABLE 2

C TO H RATIOS OF CARBON DEPOSITS FROM CIS-2-BUTENE AT 550°C

Composition (%)		C/H (wt)	C/H (atomic)	Balance to 100%
C	H			
98.50	1.65	60	5.0	+0.1[a]
98.71	1.20	82	6.9	−0.1[a]
98.52	1.69	54	4.5	+0.2[a]
96.96	1.51	63	5.3	−1.5
95.62	1.14	83	7.0	−3.2
95.81	1.41	68	5.7	−2.8
96.25	1.40	69	5.7	Average

[a] Long overnight runs, heavy carbon deposit.

In general, the reaction is autocatalytic, the final rate of deposition being dependent on reaction conditions but independent of foil pretreatment (Table 1, Fig. 2). There is good evidence to suggest that the final rate is independent of the surface of the foil, being catalyzed by nickel crystallites transported with the growing carbon. Thus the carbon deposit contains quite large amounts of dispersed nickel and, if separated from the foil, is just as good a catalyst as the original foil + carbon. Carbon itself, without nickel contaminants, is inactive.

In contrast, the initial stages of carbon deposition were very dependent upon pretreatment of the foil, as well as on reaction conditions. The most satisfactory explanation of the observations seems to be associated with the need for nucleation and growth of the new solid phase. There is evidence both from LEED and Auger work that minute amounts of carbon present in pure nickel tend to segregate and to form graphite domains on the surface above ca. 340°C (*13*, *14*). If these domains act as nuclei for carbon deposition, then heat treatment at reaction temperature would be expected to facilitate segregation and accelerate subsequent deposition. Hydrogen treatment, on the other hand, would be expected to remove such domains, and lead to retardation of nucleation and growth. Both these effects have been observed experimentally. The dependence of the induction period on temperature (an apparent activation energy of 100 kcal/mole) could then be associated with the segregation of domains or with subsequent growth processes. The activation energy for the diffusion of carbon through nickel has been reported to be ca. 35 kcal/mole (*15*), and hence the growth processes would appear to be rate determining at the early stages of reaction.

In agreement with the concept of domain separation, carbon growth does appear to originate near the grain boundaries. In addition, the separation of nickel crystallites from the surface would indicate that nucleation may also occur at grain boundaries near to the surface of the bulk nickel. Subsequent growth would lead to separation of nickel crystallites from the surface of the foil.

The process of carbon formation on nickel is undoubtedly complex, involving interrelated adsorption, diffusion, and solid state reactions. Detailed studies of the kinetics of the reaction under steady state conditions have been completed (*16*), and electron diffraction studies have elucidated the role of the carbides in the initial and steady state stages of carbon deposition (*12*).

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