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Gasification of Carbon Deposits on Nickel Catalysts

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The kinetics of the reaction of steam and of hydrogen with carbon deposited on nickel foil and on supported nickel catalysts are reported for the temperature range 820–1020 K. The rate of reaction with steam has been shown to be controlled by the diffusion of carbon through nickel. Gasification of carbon by hydrogen is governed by the rate of the surface reaction.

INTRODUCTION

Nonoxidative catalytic conversion of hydrocarbons is often complicated by the formation of carbonaceous deposits. With reactions such as steam reforming or methanation, knowledge of the kinetics of carbon formation and gasification is important for two reasons. The first of these involves the normal operation of the catalyst, where it may be possible to minimize overall carbon deposition by adjusting reaction conditions to balance the rates of formation and gasification of coke. Second, if the catalyst does accumulate significant quantities of carbon, regeneration by gasification can be optimized on the basis of detailed kinetic measurements.

Gasification of carbon on oxide catalysts is usually accomplished by high temperature oxidation with air in the presence of diluents such as nitrogen or steam (*1*). With metallic catalysts, a less reactive gas is often used, since gasification with oxygen is exothermic and may cause permanent deactivation by sintering. Gasification can still be rapid, since transition metals are active catalysts for the reaction of carbon with hydrogen or steam (*2–5*).

As part of a general program to elucidate the kinetics of the catalytic conversion of hydrocarbons over nickel-based catalysts, measurements of the rates of carbon formation during the pyrolysis/cracking of olefins have been reported (*6*). The present paper describes the kinetics of carbon removal from nickel catalysts by hydrogen and by steam.

NOMENCLATURE

D	Diffusivity of carbon in nickel.
L	Average size of nickel particles.
S	Solubility of carbon in nickel.
r_D	Calculated rate of diffusion of carbon through nickel.

EXPERIMENTAL METHODS

The experimental arrangement consisted of a microbalance (C.I. Electronics, Mk 2B) and associated flow reactor, furnace and temperature controller (±0.5 K), feed system for reactants and on-line gas chromatograph.

Both polycrystalline nickel foils and supported nickel catalysts were used. The foils, obtained from Metals Research Ltd., were of 99.7% purity, 0.1 mm thickness and geometric surface area of about 23 cm^2/g. A nickel on alumina catalyst (courtesy of I.C.I. Ltd., Agricultural Division) was prepared by soaking α-Al_2O_3 pellets

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first in aluminum nitrate melt, then in nickel nitrate melt and calcining at 720 K. A Ni/γ-Al_2O_3 catalyst was thus obtained on the α-Al_2O_3 pellet. The catalyst contained 18% Ni after reduction. Total surface area, as determined from nitrogen adsorption by the BET method, was 14 m^2/g; the metal surface area of the reduced catalyst was determined by CO chemisorption and was 0.4 m^2/g. The catalyst was crushed, sieved and the fraction 40–60 mesh (B.S.S.) used for kinetic experiments after reduction in a stream of hydrogen at 870 K. Nitrogen, hydrogen and propylene were obtained from cylinders and were of technical grade. Water vapor was produced in a pick-up bubbler system, where a carrier nitrogen stream was saturated at known temperatures. The system was calibrated by condensation and by gas chromatography.

Carbon was deposited over the nickel catalysts by pyrolysis of C_3H_6/H_2 mixtures diluted with nitrogen, at temperatures of 770–820 K (*6*). Carbons obtained over nickel foils were of surface area of about 110 m^2/g, whereas carbons deposited on the supported catalyst showed higher surface areas (133 m^2/g).

The coked catalysts were suspended from the balance arm, with powdered catalysts being placed inside a silica basket. The system was flushed with nitrogen, brought to reaction temperature and the reactants were admitted.

RESULTS

Gasification by Water Vapor

Gasification of carbon deposits, either over nickel foils or over the supported catalyst, was found to proceed at constant rates up to about 60–70% burnoff, as seen in Fig. 1 for the case of nickel foil. At low temperatures some residual carbon was left on the nickel foil, but total gasification occurred on increasing the temperature. With both catalysts, the main products of reaction were found to be hydrogen and CO_2, traces of CO being occasionally detected. The ratio of the rates of hydrogen production and of carbon consumption was found to be close to 2, so that the overall scheme,

$$C + 2H_2O \rightarrow CO_2 + 2H_2,$$

was obeyed.

The total flow rate used was always about 1 mole/hr; the partial pressure of water vapor was varied from 0.05 to 0.36 atm and the total pressure was kept constant at 1 atm by varying the flow rate of diluent nitrogen. The effect of temperature was studied over the range 820–1020 K.

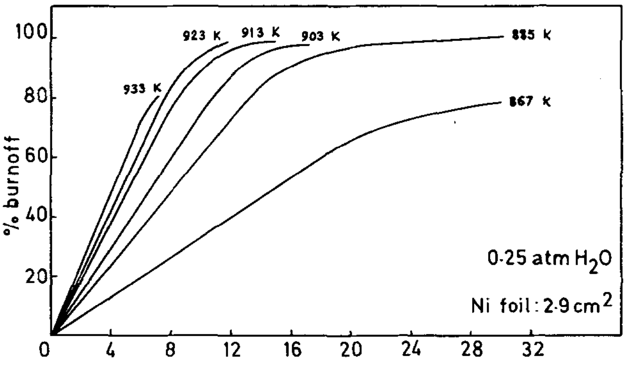

FIG. 1. Gasification of carbon deposits from nickel foils in reaction with steam at various temperatures. The amount of carbon varies between 6 and 10 mg cm^{-2}. "Burnoff" signifies the amount of carbon removed expressed as a percentage of that originally present.

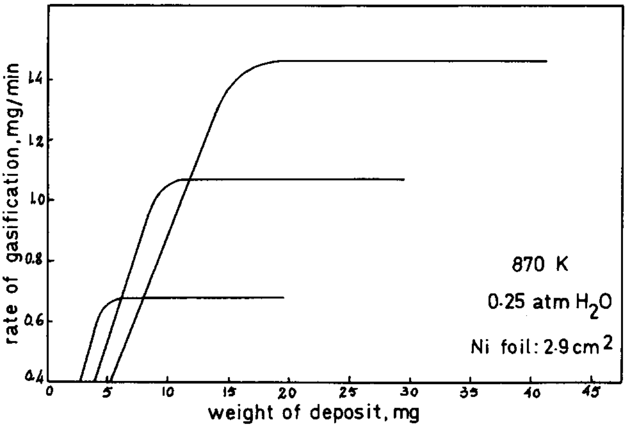

FIG. 2. Dependence of gasification rates on the amount of carbon. Reaction with steam on nickel foils.

Rates of gasification were found to be independent of the partial pressure of water vapor for both catalysts in the range studied. The temperature dependence of gasification was found to depend on the system: over nickel foils, the observed activation energy was 32 ± 2 kcal/mole, but a substantially lower value was determined for the Ni/Al_2O_3 catalysts (18 kcal/mole). In the latter case, the rates of gasification were found to be independent of the amounts of catalyst and coke present. These results suggest diffusion limitations in the case of the supported catalyst, and calculation has shown that a substantial concentration gradient may exist between the gas phase and the surface of the catalyst. With nickel foils, although gasification rates were constant throughout the burnoff (up to 70%), they were nearly proportional to the amount of carbon originally present (Fig. 2). The specific surface areas of the carbon deposits on both catalysts were found to remain constant throughout the burnoff, as shown in Table 1. Values are corrected for the surface area associated with the catalyst.

Gasification by Hydrogen

The reaction of carbon with hydrogen was much slower than with water vapor. The only observable product of reaction was methane, and the gasification showed features similar to gasification with steam, with the exception that the reaction was second order in hydrogen, in the range 0.13–1.0 atm. The same activation energy was measured for both foil (32 ± 1 kcal/mole) and catalyst (31 ± 3 kcal/mole). Once again, rates of gasification over nickel foils were found to be proportional to the amount of carbon initially present, while no such correlation was observed in the case of the supported catalyst.

Analysis of Carbon Deposits

The kinetic behavior of the gasification reactions over nickel foil, compared to the Ni/Al_2O_3 catalyst, was attributed to the

TABLE 1
CONSTANCY OF CARBON SURFACE AREA (SA) WITH BURNOFF

Catalyst	Deposit (mg)	Original SA		SA after burnoff		
		(m²)	(m²/g)	% burnoff	(m²)	(m²/g)
Ni/Al_2O_3	43.0	5.7	133	85	0.89	135
Ni foil	37.1	4.1	109	38	2.15	107

presence of metal particles in the carbon deposit (see below). An attempt was made to measure the Ni surface area in the deposits by carbon monoxide chemisorption. Although a noticeable uptake was observed, the results were inconclusive, the accuracy of the measurements being severely limited by the relatively small amounts of material available.

Carbon deposits obtained on nickel foils were then analyzed for nickel, by wet-chemistry methods. The results showed appreciable amounts of nickel in the carbon and, moreover, they revealed that the amount of nickel was nearly proportional to the weight of the carbon deposit. Eleven samples of carbon (30–120 mg deposits) were analyzed, and an average concentration of nickel of 1.6 ± 0.4 wt% was determined. Carbon deposits on supported nickel catalysts were analyzed for nickel: the amount of nickel was independent of the weight of deposit, with ca. 50–60% of the nickel on the original catalyst being transferred to the deposit.

Catalyzed vs. Uncatalyzed Gasification

The results obtained in the present system were compared with similar data from the literature for the uncatalyzed reaction, as shown in Table 2. The gasification reactions in the present system are found to be 3–4 orders of magnitude faster than the uncatalyzed reactions of carbon with H_2 or H_2O.

The catalytic nature of the gasification reactions was further established by studying the reactivity of carbon deposits after exposure to ethanethiol vapors, used to poison the nickel. Gasification with hydrogen at 1 atm and 920 K was negligible and it was found necessary to increase the temperature to 1120 K before any gasification of the carbon was observed. Extrapolation of the gasification rates to the normal operating conditions showed again a difference of about 3 orders of magnitude.

DISCUSSION

The rates of gasification of carbon over foils and supported catalysts were of the same order of magnitude. The kinetic results for the gasification of carbon by steam and by hydrogen are summarized in Table 3. Exact comparison of the results over foil and over supported catalysts is not possible for the C–H_2O system, due to diffusion limitations. These probably arise both from the geometry of the experimental system and from limitations imposed by diffusion of steam through the carbon pores to the catalyst surface (*1*).

TABLE 2

COMPARISON OF THE PRESENT RESULTS WITH REPORTED RATES FOR THE UNCATALYZED GASIFICATION OF CARBONS

	Uncatalyzed			Rate extrapolated from present work
Ref.	Carbon	Conditions	Rate	
(*10*)	Low temp char	870°C 0.9 atm H_2O	1.6×10^{-3}	3.4
(*11*)	Metallurgical coke	870°C H_2O	2.5×10^{-3}	3.4
(*12*)	Low temp char	816°C extrapolated to 1 atm H_2	7.5×10^{-5}	0.7

[a] Gasification rates expressed as: (mg C gasified)/(min mg C).

TABLE 3
GASIFICATION OF CARBON DEPOSITS[a]

	By water	By hydrogen
Nickel foil[b]	$E = 32 \pm 2$ kcal/mole zero order Rate proportional to initial carbon wt Rate constant at 923 K = 40.8 × 10^{-3} min^{-1} cm^{-2}	$E = 32 \pm 1$ kcal/mole 2nd order Rate proportional to initial carbon wt Rate constant at 923 K = 17.4 × 10^{-3} min^{-1} cm^{-2} atm^{-2}
Supported nickel catalysts	$E = 18 \pm 1$ kcal/mole Probably diffusion limitations	$E = 31 \pm 3$ kcal/mole 2nd order Rate independent of amount of carbon Rate constant at 923 K = 32.7 × 10^{-3} mg min^{-1} cm^{-2} atm^{-2}

[a] Total pressure = 1 atm; temperature range, 800–1000 K; range of water partial pressures, 0.05–0.36 atm; range of hydrogen partial pressures, 0.13–1.0 atm.

[b] Rate constants for nickel foil are referred to the geometric area of the foil.

The chemical reaction is shown with hydrogen, and diffusion is not significant. In this case, removal of carbon by both gases is catalyzed by the presence of nickel, but the dependence of rate upon the initial weight of carbon deposit was found to be different between the unsupported and supported nickel. It is instructive to discuss this in terms of the mechanism of formation of the carbons.

The kinetics of carbon deposition on nickel have been studied in some detail (*7*,*8*), and a mechanism which explains most of the observations has been advanced. Surface reaction is assumed to proceed in a series of dehydrogenation steps, leading to the formation of carbon species. These dissolve in and precipitate from the nickel, detaching nickel crystallites from the surface of the foil. Further deposition carries the nickel with the growing carbon, as shown by electron microscopic examination of the deposits (*8*).

Transportation of nickel by carbon growing on foil should result in nickel particles spread throughout the carbon, since the foil is effectively an "infinite" source of nickel. Carbon deposited on supported nickel should contain nickel only to the amount originally available on the surface of the catalyst. This prediction is confirmed by chemical analysis of the nickel content of the carbons. Since the gasification of carbon is metal catalyzed, the rate of gasification should then be proportional to the weight of carbon deposited on the foil (which contains a constant concentration of nickel) and should be independent of the weight of carbon deposited on the supported catalyst (which contains a constant amount of nickel). This was found to be the case for reaction with both hydrogen and steam (Table 3).

Some indication of the rate determining steps involved in the gasification emerges from semiquantitative analysis of the results. The carbon deposits can be expected to contain nickel crystallites of various size, but a mean size of 30 nm associated with carbon filaments (*17*) and of 70 nm associated with pyrolytic deposits (*8*,*13*) has been measured. If these particles are saturated with carbon (*6*,*8*), gasification will deplete the exposed surface and a concentration gradient will be established across the particles to act as a driving force for diffusion of carbon through nickel:

$$r_D = \frac{DS}{L}.$$

Assuming that the concentration of carbon at the nonexposed surface equals the solubility, at 923 K, $S = 5.37 \times 10^{-3}$ g cm^{-3} (*15*) and $D = 1.27 \times 10^{-9}$ cm^2 sec^{-1} (*16*). Insertion of these values gives

$$r_D(923\ \mathrm{K}) = 2.37 \text{ to } 0.98\ \mu\mathrm{g\ sec}^{-1}\ \mathrm{cm}^{-2},$$

assuming that $L = 30$ and 70 nm, respectively.

Inspection of the results summarized in Table 3 shows that gasification by steam is zero order, as would be expected if the reaction was controlled by the diffusion of carbon through nickel. Calculation of the experimentally observed rate at 923 K (1.28 μg sec^{-1} cm^{-2}) shows that good agreement is observed with prediction and supports the suggestion that the rate of gasification by steam is controlled by the diffusion of carbon through the nickel. At 873 K, the equilibrium constant for the reaction,

$$\mathrm{Ni\ (s) + H_2O\ (g) = NiO\ (s) + H_2\ (g)},$$

is 8.5×10^{-3} (*18*) and, as expected, electron diffraction showed the presence of some nickel oxide after gasification.

Gasification with hydrogen is considerably slower than with steam, and the reaction is second order. It would thus seem that the rate of reaction on the surface is rate-controlling with this gas.

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