JOURNAL OF CATALYSIS **1**, 227–234 (1962)

A Kinetic Investigation of the Reaction of Nickel Carbide with Hydrogen

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Received January 29, 1962

On heating nickel carbide in excess hydrogen at 250–300°C methane and ethane were formed in the ratio 1:0.050 and no other product was detected by gas chromatographic analysis. Reaction kinetics for the formation of both compounds followed second order kinetics where reaction rate was directly proportional to total concentration of reactant carbon in the nickel carbide and to the pressure of hydrogen (between 15 and 60 mm) in the reaction vessel. The energy of activation for methane and ethane formation were found to be 4.0 ± 0.5 and 7 ± 1 kcal/mole, respectively. A reaction mechanism is proposed which is consistent with results from cracking experiments where it has previously been suggested that nickel carbide may be an intermediate.

Many investigations (*1*) have shown that on heating reduced nickel metal in the presence of a number of carbon-containing compounds (e.g., carbon monoxide, methane) between 170 and 250°C reactions at the metal surface are accompanied by diffusion of carbon into the interior with the formation of nickel carbide, Ni_3C. A loss of carbon from a gas mixture during catalytic reactions on nickel has been reported by Moss and Kemball (*2*) and is presumably due to the same process. It is difficult, however, to prepare a pure sample of nickel carbide since its formation is accompanied by deposition of graphite on the metal surface, but the crystal structure and several chemical properties have been reported in the literature (*3, 4*). On heating nickel carbide above 300°C Hofer, Cohn, and Peebles (*1*) have shown that decomposition according to the equation:

$$Ni_3C \rightarrow 3Ni + C \qquad (1)$$

occurs by an autocatalytic reaction after an induction period during which it is believed that reaction centers are set up. Nagakura (*4*) has confirmed that decomposition occurs at high temperatures and also has shown that the hydrogenation reaction

$$Ni_3C + 2H_2 \rightarrow 3Ni + CH_4 \qquad (2)$$

reported by Bahr and Bahr (*5*) is slow compared with the carbon deposition reaction, Eq. (1), above 400°C.

The above experimental results show that carbon may be removed from nickel carbide by hydrogenation at temperatures comparable to those at which it is formed by reaction with carbon-containing compounds but at higher temperatures the disproportionation reaction becomes more important than hydrogenation. No detailed kinetic study of the hydrogenation reaction could be found in the literature and the present work was undertaken to establish whether or not the kinetics of this reaction were comparable to those reported for the disproportionation reaction. The other important reason for the present study was to compare results for the hydrogenation of nickel carbide with previous (*6*) work on the cracking of adsorbed hydrocarbons where nickel carbide has been postulated as a possible intermediate.

EXPERIMENTAL

A diagrammatic sketch of the apparatus is shown in Fig. 1. The gas handling volume A included a mercury manometer and a McLeod gauge (not shown) and was connected (*i*) to a conventional two-stage pumping system capable of giving vacua of around 10^{-6} mm Hg, (*ii*) to a storage vessel containing hydrogen purified by diffusion through palladium, and (*iii*) to the reaction vessel B. The reaction vessel could be detached at ground glass joints and connections in this section were made from capillary tubing to minimize the dead space. The Toepler pump C was of 272 ml capacity so that a very large fraction of the product gases from B ($\sim$30 ml capacity) could be quickly transferred to the gas chromatography dosing system D by a single stroke of the pump. Nickel carbide was dispersed on glass wool in B to facilitate contact between reactants.

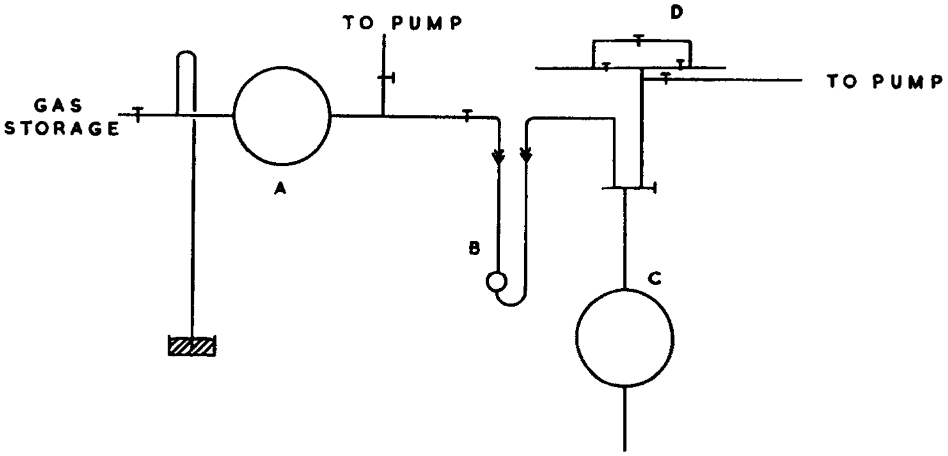


FIG. 1. Diagrammatic sketch of apparatus. Legend given in text.

After outgassing the nickel carbide for at least 60 min at reaction temperature, a known pressure of hydrogen was admitted to B (from the large volume A) where it remained in contact with the carbide for a measured time before being transferred, by the Toepler pump, for analysis in the Pye argon Chromatograph over an 80 cm 100–120 mesh B.S.S. standard screen charcoal column under conditions which have been detailed (7) for the analysis of hydrogen–methane mixtures. A new dose of hydrogen was then admitted from A and kinetic readings for methane formation were taken at 8 min intervals, the pressure of hydrogen in A being adjusted at frequent intervals to ensure that all readings of a sequence corresponded to reaction at a constant hydrogen pressure. On completion of a series of kinetic readings further analyses were made at increasing intervals until no further product was detected and the volume of methane corresponding to complete reduction determined. The retention time of the second reaction product, ethane, on the column at 23°C was some 2½ hr enabling a set of kinetic readings for methane formation to be completed before this large peak appeared. In some experiments, this necessitated the interruption of readings since no attempt was made to analyze gases while this large peak was eluted. (The sensitivity of the argon detector was very much greater to ethane than to methane.)

The kinetics of ethane formation could be studied with the same gas chromatographic column held at 100°C, using the thermostatic regulator of the apparatus as supplied, with a flow of 25 ml/min argon, and samples withdrawn for analysis at 8 min intervals. Under these conditions, hydrogen and methane peaks overlapped so that simultaneous measurement of the rate of methane formation was not possible, but satisfactory ethane peaks were eluted following the hydrogen–methane deflections of the subsequent reading, i.e., the ethane peak corresponding to reading 1 appeared after the hydrogen/methane deflections following reading 2 injected to the argon flow 8 min after reading 1, and the ethane peak of reading 2 appearing after the reading 3 hydrogen/methane peak, and so on. Cylinder ethane was used for calibrations, after it had been outgassed while chilled with liquid nitrogen and shown by gas chromatographic analysis to contain no appreciable impurity. Known pressures of ethane, measured with the McLeod gauge in A, were displaced from the known volume of the Toepler pump C into D. The accuracy of ethane calibrations was undoubtedly less than those for hydrogen and methane due to the small pressures involved; a linear relation between maximum peak height and volume of ethane injected was found over the range of interest in the present studies (0–0.0025 ml STP).

RESULTS

X-Ray Diffraction and Chemical Analysis of Nickel Carbide

The nickel carbide used in the present study was a gift from the International Nickel Company (Mond) Ltd., and had been synthesized some five years previously by reduction of nickel hydroxide pellets in hydrogen (for weeks) and then carburized with hexane. It was stored thereafter under hexane. The sample, as supplied, was stated to contain free graphite and also possibly nickel hydroxide, metallic nickel, and amorphous carbon. Chemical analysis, as part of the present study, gave 12.8% total carbon (confirming the presence of excess free carbon since nickel carbide contains 6.38% C) and 78.1% nickel (total) so accounting for 90.9% of the total, the remainder presumably being oxygen and water.

The structure of the nickel carbide, as determined from X-ray diffraction photographs, was identical, within experimental error, to that reported by Jacobson and Westgren (*3*) and by Nagakura (*4*). All the main X-ray diffraction lines listed by Nagakura (ref. (*4*), Table 1) up to the 21.2 plane were observed in the expected positions and, in addition, two further faint lines were noticed. One of these was in the position expected for the strongest diffraction line for graphite and this is readily accounted for since graphite is known to be present as an impurity. The other is close to the position expected for the 00.3 forbidden transition and could be either due to this or to an unidentified impurity. None of the lines characteristic of nickel metal or nickel oxide were observed.

After reduction of two different specimens of nickel carbide at 265° and at 320°C the resultant powder gave X-ray diffraction patterns characteristic of nickel metal and, in the case of the sample reduced at 320°C, which had been exposed to the atmosphere while at 100°C, the presence of nickel oxide was indicated but no lines characteristic of nickel carbide remained in either specimen. The faint line attributed to graphite above, did not fade on reduction.

Kinetic Experiments

All kinetic experiments were performed on samples of nickel carbide which had been exposed to the atmosphere for less than a week after removal from storage under hexane since X-ray diffraction and gravimetric measurements had shown that negligible oxidation occurred in this period.

The reduction of nickel carbide with hydrogen in the temperature range 250–350°C resulted in the formation of methane and ethane, the former being in greater quantity than the latter; there was no evidence for the formation of propane or higher hydrocarbons. Throughout the study ethane was invariably formed under all conditions where reduction yielded appreciable quantities of methane, the only exception being in instances where the product gases had been allowed to remain in contact with nickel carbide for some hours when little or no ethane remained, but on resumption of withdrawal of readings at more frequent (4 or 8 min) intervals, ethane again appeared as a product.

The total volume of methane evolved on completion of the reduction reaction was directly proportional to the weight of nickel carbide reduced, as shown in Fig. 2, and was independent of mechanical grinding alone or in a mixture with added graphite. Providing outgassing periods were short, around 1 hr at reaction temperature, the volume of methane evolved was independent of temperature between 250° and 350°C, but if more vigorous outgassing conditions were employed, e.g., 2 hr at 365°C or overnight at 320°C, the total volume of product methane was very much reduced. The volume of ethane produced simultaneously was also directly proportional to the weight of carbide reduced and independent of temperature between 250° and 300°C, though the scatter of results (see Fig. 2) was somewhat greater than for methane. The total volume of ethane produced was independent of grinding or admixture with graphite but decreased somewhat with increasing reaction temperature above 300°C. The ratio of total volumes of product methane to ethane was 1:0.050 between 250° and 300°C.

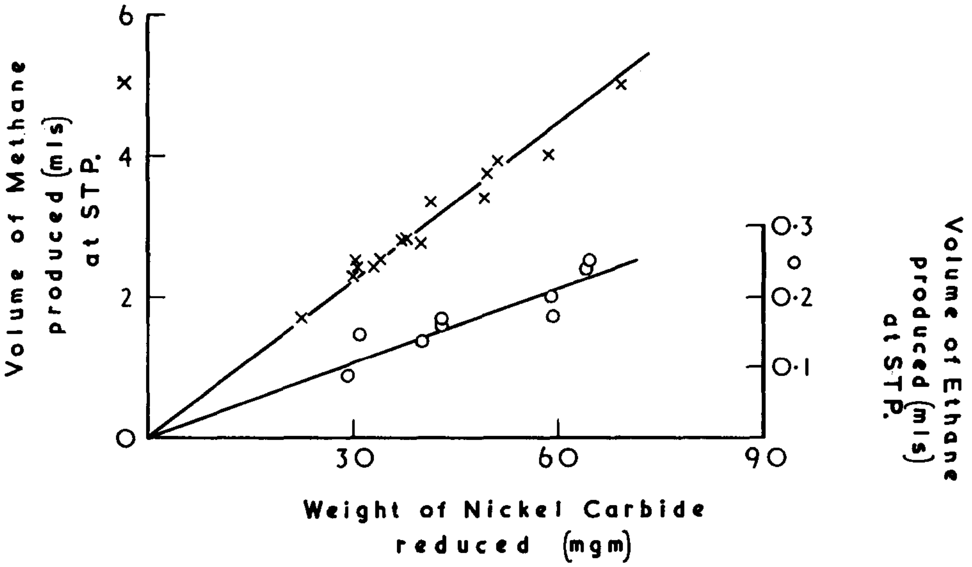


FIG. 2. Plots of volume of methane (x) and ethane (o) (ml STP) given on completion of reaction between hydrogen and nickel carbide 250–300°C.

Kinetics of methane formation. When samples of nickel carbide, which had been lightly crushed to break the larger aggregates, were heated in hydrogen between 250° and 350°C methane was formed by a reaction which was deceleratory throughout. Kinetic readings for reaction at constant hydrogen pressure were tested for obedience to two kinetic equations:

$$1 - (1 - \alpha)^{1/3} = k_1 t \qquad (3)$$

$$\log\left(\frac{1}{1 - \alpha}\right) = k_2 t \qquad (4)$$

where α is the fractional decomposition after time t. Equation (3) is derived on the assumption that a reaction interface is set up at the surface of each particle and progresses into the reactant. Equation (4) assumes the rate of reaction to be proportional to the quantity of reactant remaining. Equation (3) was approximately obeyed within the range $0.05 < \alpha < 0.55$ while Eq. (4), which was a more satisfactory fit to the kinetics (Fig. 3), was obeyed over the larger range $0.1 < \alpha < 0.9$. From a series of experiments the following kinetic characteristics of the reduction were established:

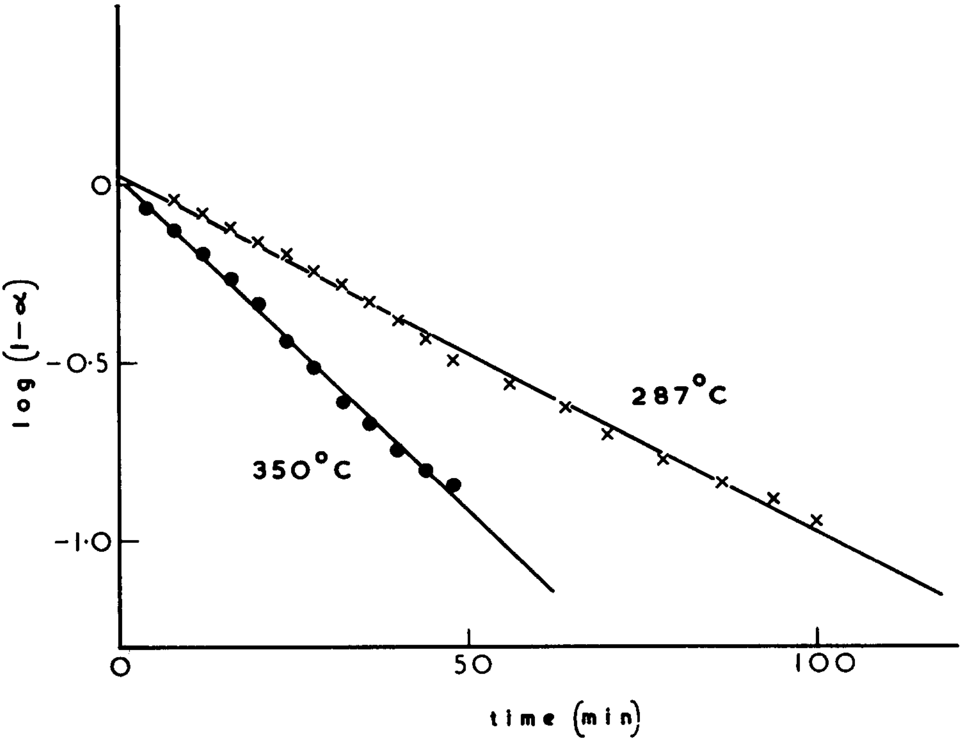


FIG. 3. Pseudo-first-order plots for methane evolution for reaction of nickel carbide in a constant pressure of hydrogen at 287°C (×) and 350°C (●).

1. The rate constant of reaction at any temperature (either k_1 or k_2) was directly proportional to the pressure of hydrogen admitted in each dose between 15 and 60 mm.

2. The energy of activation for reduction in hydrogen (50 mm pressure) was 4.5 ± 0.5 kcal/mole using rate constants derived from Eq. (3) while from the temperature coefficient of k_2 this was 4.0 ± 0.5 kcal/mole.

3. The reduction of carbide thoroughly ground in pestle and mortar gave identical kinetic characteristics to those observed for the lightly ground material, and an identical energy of activation, but reaction rate (as determined from both k_1 and k_2) was slower by a reduction of 0.35 in the logarithm of the Arrhenius pre-exponential factor.

4. Large pellets of material (2 mm in diameter) reacted at a rate identical with that of lightly crushed material (< 0.2 mm diameter particles).

5. Samples crushed with graphite reacted at a rate intermediate between the lightly and more vigorously crushed material.

Kinetics of ethane formation. The kinetic characteristics of this reaction were identical with those for methane formation except: (1) the obedience to the kinetic equations was less satisfactory than that for the methane formation; this may be ascribed to reduced accuracy of calibration. It was clear, however, that the same equations were obeyed over similar ranges of α, and (2) the energy of activation was 7 ± 1 kcal/mole.

Other experiments. Nickel carbide heated at 300°C, in vacuo, desorbed very small quantities of hydrogen, methane, carbon monoxide and carbon dioxide, sufficient to be only just detected with the analytical technique used. Under normal reaction conditions, these would be evacuated during outgassing.

The reaction rate for methane formation in 50 mm hydrogen at 100°C was so slow that the volume formed in one hour could only just be detected. After outgassing nickel carbide for 2 hours at 460°C no methane was detected in a subsequent reaction in 50 mm hydrogen at 290°C. No methane was detected on heating a 56:44 by weight nickel oxide:graphite mixture under normal reaction conditions at 290°C. A mixture of fine nickel powder with 3.7% by weight added graphite crushed in pestle and mortar, when heated under normal reaction conditions, evolved small amounts of methane corresponding to the reduction of only 1% of the graphite of the mixture by a reaction which had a small energy of activation (~3 kcal/mole).

Adsorption of hydrogen at 0°C on a sample of reduced nickel carbide, which had been outgassed overnight at 300°C, was too small to be measured in the present apparatus.

Discussion

The present results are entirely consistent with the suggestion by Bahr and Bahr (*5*) that methane is formed on reduction of the carbon in the nickel carbide according to Eq. (2). This is supported by the observed linear relation between volume of methane produced and weight of nickel carbide reduced and also by comparison of the weight of carbon removed on complete reduction (3.90% weight of original sample) with 4.98% theoretical total weight of carbon as carbide if the total weight of nickel in the sample were all present as nickel carbide, when due allowance is made for the evidence that an appreciable fraction of the nickel in the original material is present as oxide. A strict quantitative test of Eq. (2) cannot, however, be made from the data obtained in the present study but it adequately accounts for the results obtained.

The present results also support the suggestion of Nagakura (*4*) that the hydrogenation reaction is reduced in importance at higher temperatures due to the onset of the direct decomposition reaction (*1*). Hofer, Cohn and Peebles (*1*) have shown that the induction period for the onset of the decomposition reaction at 355°C was 100 min which is in very satisfactory quantitative agreement with observations from the present work that the reduction reaction, after the sample had been outgassed at 355°C for 60 min evolved the same volume of methane, per unit weight of sample, as that formed in reaction at lower temperatures, whereas after 120 min outgassing at 365°C resulted in the evolution of only some 20% of the expected volume of methane. It is clear, however, that once the reaction centers have been established, the elemental carbon deposited can no longer react quantitatively with hydrogen and this was supported by the observations: (*i*) addition of graphite with grinding did not change the final yield of methane and (*ii*) a negligible fraction (~1%) of the graphite ground with pure nickel powder was hydrogenated to methane under normal reaction conditions. It is concluded, therefore, that free carbon on nickel metal is not appreciably reduced under the hydrogenation conditions studied here, again supporting the belief expressed above that methane and ethane are only formed from carbidic carbon at these temperatures.

In contrast to the decomposition reaction (1) the kinetics of the reduction reaction (2) are not consistent with a mechanism based on the formation and growth of nuclei, since no induction and acceleratory periods are observed. Two alternative reaction schemes may therefore be considered, (a) a "contracting cube law" where the product is formed on the surface of the reactant particle and the latter therefore decreases in size with time —this mechanism has been discussed by

Delmon (*8*) for the reduction of nickel oxide—and (b) a "catalytic" or "diffusion" model where the carbon atoms in the bulk of the crystal are in equilibrium with surface species and the latter may be replaced during hydrogenation by diffusion from the bulk. Model (a) is not satisfactory since Eq. (3) holds over a relatively limited range of α. Furthermore, the rate of reduction (from both k_1 and k_2 is *reduced* on grinding showing that the latter stages of reaction are *not* opposed by increasing difficulty of diffusion of hydrogen to, and methane from, the reactant interface through an increasing thickness of product layer. No attempt has been made, therefore, to fit the results to any modified form of Eq. (3), such as that recently proposed by Carter (*9*). Also, the effect of particle size and shape together with the effect of the free graphite on Eq. (3) for the particular system studied here cannot be adequately estimated.

The experimental data are consistent with a model for the methane and ethane formation reactions in which carbon atoms in the bulk are in equilibrium with those on the surface and the latter may be removed on hydrogenation and are replaced by diffusion from the interior. The reverse reaction, diffusion of carbon from adsorbed radicals into the bulk, with the formation of nickel carbide, has been shown by Moss and Kemball (*2*), and other workers, to occur at these temperatures. The kinetic results may be explained by a model which assumes that there is a direct proportionality between the concentration of the adsorbed radical which is hydrogenated to methane $[CH_x]$ and the total quantity of carbon in the sample which may be hydrogenated to methane [C], so that

$$d[CH_4]/dt = k_3[CH_x][H]^y = k_4[C][H]^y$$

and for reaction in constant pressure of hydrogen the pseudo first order equation is obeyed

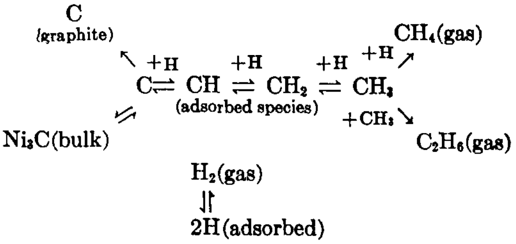
$$d[CH_4]/dt = k_5[C]$$

The relative concentrations of the various possible surface radicals (CH_3, CH_2, CH, C) and also the rate of methane formation may all be influenced by the concentration of adsorbed hydrogen atoms [H], as has been discussed elsewhere (*6*), and it seems reasonable to suppose that the concentration of adsorbed hydrogen atoms controls both the concentration of the carbon-containing reactant in the rate-controlling step $[CH_x]$ and the rate at which this reacts to form methane, so accounting for the observed direct proportionality of reaction rate on hydrogen pressure and reaction kinetics accurately obey the second order equation:

$$d[CH_4]/dt = kP_{H_2}[C] \qquad (5)$$

Thermodynamic calculations show that the volume of ethane produced is very much greater than the equilibrium amount expected from the methane at these temperatures, hence the concentration of carbon on the surface must be large and the linking between carbon atoms favored. The decrease in proportion of ethane in products at temperatures above 300°C may be ascribed to cracking which is known (*10*) to occur at around 200°C on a nickel-kieselguhr catalyst. The volume of product ethane has been omitted from the semi-quantitative calculations given above for testing Eq. (2) but the close agreement between the kinetics of methane and ethane formation leave little doubt that they are simultaneously evolved from a common intermediate.

The reactions postulated above can be conveniently summarized in the following scheme:



In excess hydrogen it is believed that negligible readsorption of methane occurs but above 300°C readsorption and cracking of ethane becomes appreciable.

The decrease in the methane (and ethane) formation reaction rate with crushing may be ascribed to two possible causes, either the total surface area of the sample is reduced on cold working through joining (sintering) of small crystallites, or the destruction of the most active parts of the surface for methane desorption on grinding. The former suggestion is considered the more probable since the latter implies an increase in the activation energy rather than a change in the frequency factor as was observed. The effect of added graphite is probably to reduce the degree of cold working on grinding since graphite-containing material gave rate constants falling between results for crushed and uncrushed material and these results showed greater scatter than either the crushed or the lightly crushed material.

The above reaction scheme entirely supports the suggestion that nickel carbide is a possible intermediate in methane formation in the cracking reactions studied elsewhere (*6*) since both reactions show the following characteristics in common:

1. Reactions occur in the same temperature range.

2. Kinetic readings for both reactions accurately obey the pseudo first order equation over a very large range of α in constant pressure of hydrogen.

3. Pseudo-first-order rate constants were directly proportional to hydrogen pressure so that both reactions obeyed the same Eq. (5). The pressure range studied in the present work was higher than in the cracking studies; this was necessary to give a reaction rate suitable for study and clearly results from the very small surface area of nickel carbide compared to the high surface area of the nickel/silica catalyst.

4. Low energies of activation. The energy of activation for methane formation from nickel carbide (4 kcal/mole) is greater than that observed in cracking work (0 or small negative values). This difference may be ascribed to a different temperature dependence of the equilibrium concentration of carbon atoms adsorbed on the surface to that present in the bulk for nickel carbide as compared to the nickel-silica catalyst. This is reasonable since each nickel carbide sample was subjected to a single reduction reaction and then discarded whereas the surface of the nickel-silica catalyst had been annealed to give a surface of considerable stability after many cycles of carbide formation followed by reduction.

The large surface area, with consequent lower concentration of surface carbon atoms in addition to the increased probability of readsorption adequately accounts for the absence of ethane as product from the cracking experiments (*6*).

It is concluded, therefore, that the reduction of nickel carbide does not follow kinetic laws characteristic of reaction at a solid/solid interface but probably takes place by hydrogenation of radicals at the existing surface which are in equilibrium with carbon atoms of the bulk phase. Also, the reaction kinetics are consistent with the supposition made in previous studies of the cracking reactions of hydrocarbons (*6*), that carbon may diffuse into the interior of nickel particles and subsequently reappear at the surface where it may be hydrogenated to methane.

ACKNOWLEDGMENTS

The author would like to thank Mr. P. D. Wilmot and the International Nickel Company (Mond) Ltd. for the gift of the sample of nickel carbide, and Miss I. Woodward for her skilled assistance in obtaining and interpreting the X-ray diffraction patterns.

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