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The Reversible Decomposition of Methane on a Ni/SiO$_2$ Catalyst

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The interaction of CH$_4$ with a silica-supported nickel catalyst is studied at temperatures from 30 to 350°C, both in continuous-flow and pulse-flow experiments. Even at 30°C chemisorption is observed; the apparent activation energy for the chemisorption is estimated at 6 kcal mole^{-1}. At temperatures above 175°C the methane which is adsorbed on the Ni catalyst dissociates completely into adsorbed carbon atoms and hydrogen. The hydrogen released shifts the equilibrium $CH_4(g) \rightleftarrows C(ads) + 4H(ads)$ to the left side. The reactivity of the carbonaceous deposit with hydrogen is also investigated. At all temperatures in the range 30 to 450°C the only product of the exothermic reaction is methane. The reactivity passes through a maximum at 200°C and strongly decreases at temperatures above 300°C.

INTRODUCTION

Supported catalysts, vapour-deposited films, and single crystals have been used to study the interaction of methane with nickel surfaces. Working with single crystals Schouten *et al.* (*1, 2*) established the interaction to be strongly affected by the atomic structure of the surface. At 200°C the carbon content of a nickel (110) surface increased rapidly on exposure to methane, whilst that of a (100) surface rose appreciably more slowly. A nickel (111) surface, on the other hand, did not show a measurable reaction with methane even at more elevated temperatures. Experiments with supported catalysts and vapour-deposited films have indicated that at small hydrogen coverages methane chemisorbs dissociatively on nickel surfaces. Carbon or carbon–hydrogen complexes remain adsorbed; the hydrogen set free is either chemisorbed or desorbs as molecular hydrogen depending on the temperature. On Ni films Frennet (*3*) did not observe chemisorption below 100°C. Wright *et al.* (*4*) found their nickel films to decompose methane only above 170°C. Gaidai *et al.* (*5*) established that a silica-supported Ni catalyst took up a marked amount of CH$_4$ at 28°C and pressures between 45 and 200 Torr.

The reactivity with hydrogen of the adsorbed species resulting from the interaction of methane with nickel has not been extensively studied hitherto. Gaidai *et al.* (*6, 7*) reported on this interaction studied in a limited temperature range (320 to 420°C). Rabo *et al.* (*8*) investigated the reaction of hydrogen with carbon deposited on a Ni/silica catalyst by the reaction $2CO \rightarrow C + CO_2$. After CO disproportionation on a Ni/alumina catalyst at 500 ± 50 K, McCarty and Wise (*9*) distinguished four types of surface carbon with different reactivity towards H$_2$. McCarty and Wise and Rabo *et al.* agree that the reactivity sharply drops when the carbon is heated at temperatures above 300°C.

This paper deals with the decomposition of methane on a Ni/silica catalyst and with the reaction of the adsorbed reaction products with hydrogen. The reactions have been studied in fixed-bed reactors. Pulse- and continuous-flow experiments have been carried out at temperatures between 30 and 450°C.

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EXPERIMENTAL

The catalyst was prepared by precipitation of Ni(II) ions from an aqueous solution onto a suspended silica support (Aerosil, Degussa, 380 $m^2 g^{-1}$) by means of urea decomposition at 90°C. This preparation procedure has been described in detail by Van Dillen *et al.* (*10*), Hermans and Geus (*11*), and Vermeulen *et al.* (*12*). The nickel-to-silica weight ratio of the catalyst was 1.0. The loaded carrier evacuated at 180°C showed a surface area of 256 $m^2 g^{-1}$ (BET, N_2). The catalyst dried at 120°C was pressed (800 kg cm^{-2}) and cut into small bodies of dimensions between 1.5 and 2.5 mm. Dehydration and reduction were carried out in the reactor. Dehydration was effected in a flow of dry nitrogen at 350°C and reduction in a flow of 10% hydrogen in nitrogen for at least 80 hr at 450°C. The degree of reduction was determined thermogravimetrically and found to be 70%. The specific nickel surface area was calculated from the extent of hydrogen chemisorption at 30°C on a freshly reduced and evacuated catalyst. The H_2 isotherm was nearly flat at pressures above 10 Torr (1 Torr = 133.3 N m^{-2}); from the amount of hydrogen adsorbed at 250 Torr the specific nickel surface area was calculated to be 34 $m^2 g^{-1}$ (reduced) catalyst. For the surface density of Ni a value of 1.5×10^{19} atoms m^{-2} was taken.

Pulse- and continuous-flow experiments could be done with the apparatus used. Nitrogen and hydrogen, both taken from cylinders, were dehydrated by Linde molecular sieve, type 4A. Nitrogen was deoxygenated by BASF catalyst R-3-11 (BTS catalyst), whereas hydrogen was deoxygenated by a Baker "deoxo-" catalyst (Pd/alumina). The reaction gas consisting of 10.2% CH_4 and 89.8% N_2 was supplied by Matheson; impurities were less than 70 ppm. With all gases a constant mass-flow rate was obtained by means of pressure and flow controllers. The gas flow through the reactor was always upwards. The reactor was a cylindrical tube of quartz with an inside diameter of 2.0 cm and a length of 60 cm. With the large catalyst bed (16.3 g catalyst; height 12.0 cm) the temperature was measured at six different places at the axis of the reactor tube. The temperature of the small bed (0.9 g catalyst; height 1.5 cm) was measured only in the center of the bed.

The gas phase was analysed by a Perkin–Elmer F 17 gas chromatograph, equipped with a Porapak Q column, length 1.8 m, diameter 4 mm. Nitrogen was used as the carrier gas with a flow rate of 40 ml min^{-1}. A hot-wire detector (HWD) in series with a flame ionization detector (FID) was employed. A bypass allowed determination of the composition of the gas phase before entering the reactor. In continuous-flow experiments every 5 min a sample of the reactor effluent was injected into the gas chromatograph column by means of an automatic sample valve. In the pulse-flow experiments another sample valve was used to pulse a known volume of gas (1.5 ml STP) into nitrogen carrier gas (50 ml min^{-1}) flowing through the reactor. In these experiments the product gas was analysed without passing through the separation column. The FID detected mainly methane and the HWD both methane and hydrogen. The column had been used previously to ascertain that hydrogen reacted with deposits on the catalyst only to methane.

RESULTS

Both a small and a large catalyst bed have been used in the pulse experiments. Since with a small bed the peaks are less broadened, the conversion can be measured more accurately. Moreover, the variations of the partial pressures within the catalyst bed are smaller.

The small bed contained 0.9 g of unreduced nickel-on-silica catalyst. The length of the catalyst bed was 1.5 cm (diameter 2.0 cm). The pretreated and reduced catalyst exposed a nickel surface area of 24 m^2. At different temperatures a pulse of methane of 0.15 ml STP (1.5 ml 10.2 vol% CH_4 in N_2)

was passed through the catalyst bed. If one methane molecule occupies seven sites on dissociation, about 1.9 ml STP of methane is required to saturate the nickel surface. The pulse of 0.15 ml STP hence is far below the amount that will saturate the surface. The conversions of the methane pulses have been collected in Table 1. The pulse was nearly completely chemisorbed at 300°C, whilst even at 30°C chemisorption occurred. An estimate of the activation energy for chemisorption (see Table 1, temperatures of 30 to 200°C), based on a first-order reaction, leads to a value of 6 kcal mole^{-1}. This agrees well with the value of 7 kcal mole^{-1} found by Gaidai *et al.* (*5*). At temperatures below 200°C the gas flowing out of the reactor did not contain hydrogen, whereas at 350°C the amount of hydrogen evolved was about twice the amount of methane in the pulse. At 350°C chemisorption of CH_4 thus produces surface carbon and gaseous hydrogen.

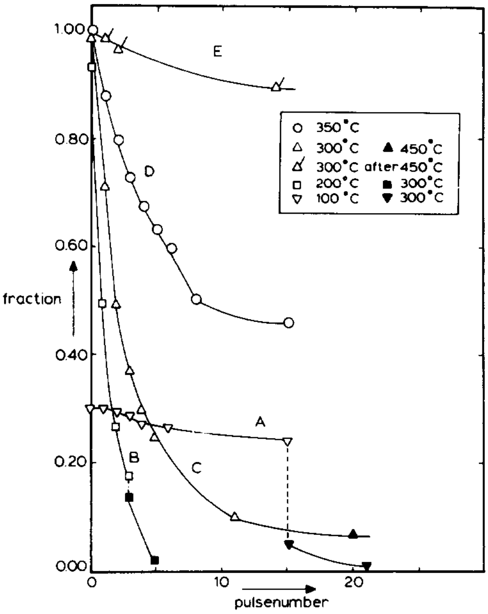

FIG. 1. The fraction of one pulse of methane remaining on the surface as a function of hydrogen pulse number. (A) CH_4 adsorbed at 100°C. (B) CH_4 adsorbed at 200°C. (C) CH_4 adsorbed at 300°C. (D) CH_4 adsorbed at 350°C. (E) CH_4 adsorbed at 300°C and subsequently kept at 450°C for 1.2 hr in a nitrogen flow. (---) Temperature rise in a nitrogen flow without hydrogen pulses.

TABLE 1

Conversion of CH_4, in Pulse-Flow as well as in Continuous-Flow (after 20 min) Experiments, as a Function of the Temperature

Temperature (°C)	Conversion (%)	
	Continuous flow	Pulse flow
30	—	7
100	—	30
175	0.3	—
200	—	93
250	1.6	—
275	2.0	—
300	3.0	99
320	5.0	—
350	10.0	100

After passing a methane pulse through the catalyst bed hydrogen pulses (1.5 ml STP H_2) were admitted at the same temperature. Unless indicated otherwise the interval between two pulses was at least 30 min. Gas chromatographic analysis showed the reaction with hydrogen to lead exclusively to methane; no higher hydrocarbons were found. It was observed that the pulsed hydrogen reacted relatively slowly. When hydrogen was pulsed at short intervals (about 2 min) the second pulse produced more methane than the first; with subsequent pulses the methane production gradually dropped. In Fig. 1 the carbon content of the catalyst surface, expressed as the fraction of the initially pulsed volume of methane, is represented as a function of the hydrogen pulse number. When hydrogen pulses were admitted to the catalyst at intervals of 2 min, only the resultant of these pulses is indicated in the figure. It can be seen that the species deposited at 200°C were the most reactive towards hydrogen. At 100°C reaction of the deposit appeared to be limited; however, when after a number of hydrogen pulses the temperature of the catalyst was raised to 300°C in a nitrogen flow, a considerable amount of methane was evolved. The experiment represented in

TABLE 2

Reactivity of Carbon Deposited at 300°C by One CH_4 pulse

Gas admitted	Temperature (°C)	Fraction of CH_4 pulse recovered (%)	Fraction of CH_4 pulse adsorbed (%)
CH_4, pulse	300	0.1	99.9
N_2, flow	300 → 30	—	99.9
H_2, pulse	30	0.1	99.8
H_2, pulse	30	0.1	99.7
H_2, pulse	30	0.1	99.6
H_2, 12 pulses	30	0.5	99.1
H_2, flow (10% in N_2)	30	1.9	97.2
N_2, flow	30 → 100	1.3	95.9
N_2, flow	100 → 300	84.0	11.9

Table 2 shows an analogous behavior with a larger amount of deposited carbon.

It was found that at least 95% of the deposit obtained below 350°C reacted to methane on passing a flow of hydrogen through the catalyst bed at temperatures up to 450°C. As shown in Fig. 1, the reactivity of the species deposited at 350°C is smaller. Even a flow of hydrogen at 450°C left 42.8% of the methane dose adsorbed on the catalyst. To establish whether a rearrangement of the adsorbed carbon proceeds above 350°C, the following experiment, which is also represented in Fig. 1, was carried out. A methane pulse admitted to the catalyst at 300°C reacted completely. The catalyst was subsequently kept in a nitrogen flow at 450°C for 1.2 hr. As shown in Fig. 1, 9% of the deposited carbon reacted at 300°C to methane with 14 H_2 pulses. A hydrogen flow at 450°C still left 85.7% of the methane pulse on the catalyst. Since an increase in temperature to 450°C in a flow of hydrogen always led to a rapid reaction of the deposited carbon, a relatively slow rearrangement of the carbon deposit must proceed at 450°C. This was also observed by McCarty and Wise (*9*) at temperatures above 600 K. Alternatively the decrease of the reactivity of the carbon deposit may be due to a slow diffusion of carbon into the bulk of the nickel crystallites. This was observed also by Schouten *et al.* (*2*) on Ni (110) at temperatures above 300°C.

The above reaction of adsorbed hydrogen with deposited species was apparent from the methane production brought about by raising the temperature in a nitrogen flow to 300°C. To establish the amount of hydrogen adsorbed by the catalyst at different temperatures, pulse experiments were done with the large catalyst bed. The large reactor was loaded with 16.25 g of unreduced catalyst. After pretreatment and reduction the catalyst exposed a nickel surface area of 435 m^2. Hydrogen remaining on the catalyst after the reduction was removed by passing nitrogen through the catalyst at 450°C for 1 hr. Subsequently the catalyst was brought to the measuring temperature and an automatic sample valve started to dose every 2 min a hydrogen pulse of 1.5 ml STP to the catalyst. During the initial hydrogen pulses the heat conductivity detector gave no response. After a number of pulses that depended on the temperature, the detector showed a continuous signal that gradually rose to a constant value. In Fig. 2 the amounts of hydrogen admitted when the heat conductivity detector had reached 50% of the final steady-state signal are represented as a function of temperature. At 25°C this amount is 73 ml STP. From static adsorption experiments at

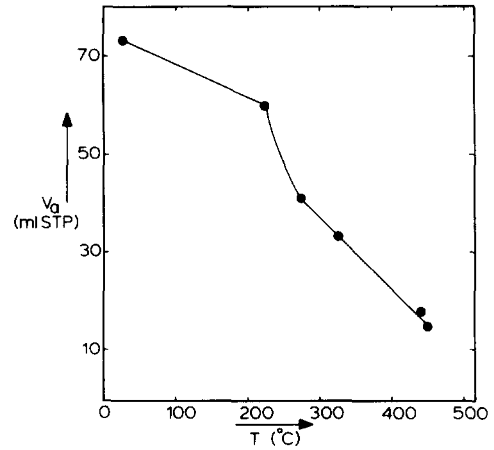

FIG. 2. The amount of pulsed hydrogen retained by the catalyst (V_a) as a function of temperature.

30°C we know that the surface is almost completely covered at a hydrogen pressure of 14 Torr, the mean pressure during the continuous addition of H_2 pulses. Full coverage of the surface would correspond to 121.8 ml STP. We ascribe the extent of adsorption being smaller than full coverage to a relatively slow diffusion of hydrogen through narrow pores in the catalyst filled with nitrogen. An appreciable amount of hydrogen therefore will be taken up after the detector signal has reached 50% of the final value. Since at more elevated temperatures the rate of transport increases and the amount of hydrogen to be adsorbed and thus to be transported drops, the equilibrium coverage will be more closely approximated. Figure 2 shows the amount of hydrogen to drop more rapidly above 225°C. In a separate experiment it was established that hydrogen, adsorbed at 25°C, desorbed in two clearly separated steps during heating in a nitrogen flow: two broad maxima were found at 130 and 280°C (peak area 1 : 3).

Continuous pulsing was also done with methane at 350°C; doses of 0.15 ml STP methane (10% CH_4 in N_2) were admitted to the large catalyst amount at a frequency of 1 pulse per 2 min. The catalyst adsorbed the first 30 pulses completely. After about 50 pulses an apparently steady state was reached in which 65% of each methane dose was decomposed. In the steady state the hydrogen evolved ($2x$ ml) corresponded to the amount of methane that disappeared (x ml).

In continuous-flow experiments a flow of 10.2% CH_4 in N_2 (40 cm^3 min^{-1}) was passed through the large catalyst bed. The catalyst had previously been freed from adsorbed hydrogen in a flow of nitrogen at 450°C. Figure 3 shows the conversion of methane as a function of time with the catalyst kept at 350°C. It can be seen that the conversion gradually drops to an apparently steady state level of about 3%, which is much lower than the steady-state level measured in continuous-pulse experiments. In the steady state the amount of H_2 evolved was about twice the amount of CH_4 that disappeared. The conversion of methane was also determined at lower temperatures. The initial rapid drop in conversion was less pronounced at these temperatures. Conversions measured after 20 min have been collected in Table 1. In the steady state no marked conversion was found at temperatures below 200°C. When the temperature of the catalyst bed was raised in a flow of

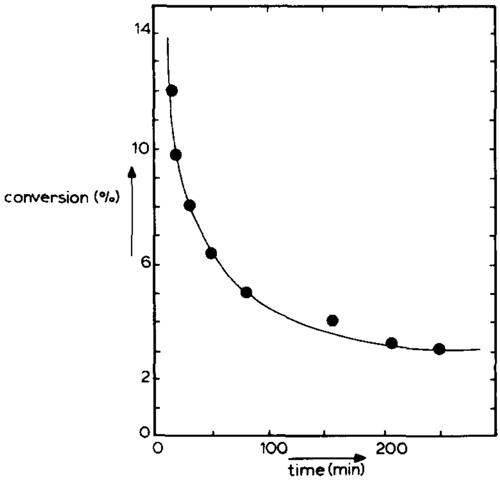

FIG. 3. Time dependence of CH_4 conversion in a continuous-flow experiment at 350°C.

the CH_4/N_2 mixture ($T > 200°C$), the CH_4 content of the reactor effluent temporarily increased. As soon as the more elevated temperature was reached the CH_4 content dropped to a value below that measured at the lower temperature, in agreement with Table 1. The hydrogen content of the product gas also showed a maximum during a temperature rise, eventually reaching a value that corresponded to the higher CH_4 conversion.

Finally, after a continuous-flow experiment at 350°C a flow of pure nitrogen was passed through the reactor kept at 320°C. The CH_4 content of the reactor effluent was found to drop more rapidly than that of hydrogen. After 3 hr the hydrogen content was negligible. Next a flow of 10% of hydrogen in nitrogen was passed through the reactor. Methane was being formed in an exothermic reaction that proceeded inhomogeneously in the catalyst bed: the thermocouple at the bottom of the reactor showed an instantaneous temperature rise of 10°C. After 1 min an increase in temperature of only 2°C was observed in the center of the catalyst bed, whereas the temperature in the upper half of the bed did not show any increase at all.

DISCUSSION

The extent of reaction of CH_4 in the continuous-flow and pulse experiments is clearly different. The most plausible inference is to ascribe the more rapidly decreasing conversion in the continuous-flow experiments to a more rapid poisoning of the catalyst by deposited carbon. However, the amount of carbon taken up when the conversion strongly drops is too small to poison the nickel surface considerably. At 350°C the hydrogen liberated from the chemisorbed methane desorbs almost completely. When we assume that a carbon atom occupies three sites, the large catalyst bed may decompose 75 ml STP CH_4.

Using a flow of about 4 ml CH_4 min^{-1} this would last for about 19 min. However, Fig. 3 shows the conversion to drop from the beginning on wards. We therefore ascribe the decreasing conversion to adsorbed hydrogen, causing a shift to the left side of the equilibrium

$$CH_4(g) \rightleftarrows CH_{(4-x)}(ads) + x\,H(ads) \quad \text{with } 0 < x < 4.$$

The methane conversion is thus not only determined by the temperature, but also by the hydrogen surface coverage. In the pulse experiments with the small catalyst bed the hydrogen surface coverage always was small. It may be seen from Table 1 that in these experiments the catalyst reacted with methane even at low temperatures. The hydrogen adsorption experiments indicated a slow transport of hydrogen through the catalyst bed: continuous pulsing of hydrogen gave rise to a continuous detector signal, in which no separate pulses could be distinguished. The broadening and subsequent overlap of the hydrogen pulses are due to many adsorption–desorption steps of the hydrogen molecules. The slow transport of hydrogen out of the catalyst bed causes the hydrogen surface coverage in the continuous-flow experiments to be high, and thus the CH_4 conversions to be low (Table 1). At temperatures below about 200°C the hydrogen surface coverage builds up so rapidly that the CH_4 conversion drops too fast to be recorded reliably. In continuous-pulse experiments hydrogen is partly removed between successive CH_4 pulses. This leads to the intermediate value of the CH_4 conversion, 65%, at 350°C. When hydrogen was admitted to the small catalyst bed after chemisorption of one dose of CH_4, the second pulse resulted in a larger production of CH_4 than the first. This is also explained by the slow transport of hydrogen: when the first pulse is still in the catalyst bed the second pulse raises the hydrogen pressure appreciably and shifts the above equilibrium to the left side. Since during hydrogen pulses the amount of rapidly reacting carbon decreases, subsequent pulses lead to a smaller production of methane.

The limited transport rate of hydrogen in the catalyst bed also brings about an inhomogeneous distribution of carbon. This was evident from the locally different temperature rises recorded when hydrogen was passed through the catalyst after chemisorption of methane in a continuous-flow experiment at 320°C. The carbon appeared to be deposited mainly at the bottom of the reactor. When at a temperature above 300°C methane is introduced into the reactor, the absence of hydrogen causes the reaction to be rapid at the bottom of the catalyst bed. Hydrogen resulting from the reaction slowly migrates to the top of the bed and inhibits the chemisorption of methane above the first layer of the catalyst particles. After the bottom layer has been completely covered, the supply of hydrogen falls and the reaction may proceed at the next layer. As a result the decomposition takes place within a relatively narrow zone that migrates through the catalyst bed. The width of the zone depends on the rate of supply of methane; a lower rate of supply causes the zone to be more diffuse.

From Fig. 1 and Table 2 it may be seen that heating the carbon-containing catalyst to 300°C in a nitrogen flow, after chemisorption of several H_2 pulses at a lower temperature, resulted in a considerable evolution of methane. This particular production of CH_4 was observed in the temperature range 100 to 300°C in which also the greater part of hydrogen was found to desorb from the catalyst surface.

We therefore conclude that the production of CH_4 is due to a transport of gaseous hydrogen to the nickel surfaces where carbon has been deposited. As a result, not only H_2 but also CH_4 desorbs from the catalyst surface. This also explains the temporary increase of both the CH_4 and the H_2 contents of the reactor effluent when the temperature of the catalyst is raised in a flow of the methane–nitrogen mixture.

The results of this work have shown that methane readily reacts with the nickel catalyst, provided the hydrogen surface coverage is low. Most probably the different reactivities of nickel catalysts, nickel films, and nickel single crystals, as mentioned in the Introduction, are due to a different fraction of reactive crystallographic planes in their surfaces. As Schouten *et al.* (*1, 2*) established a large difference in reactivity of the nickel (111) and (110) surfaces, the proportion of planes of a different reactivity must strongly affect the interaction.

In the steady state, which was observed in continuous-flow experiments above 175°C, it was found that methane, as far as it was decomposed, dissociated completely into adsorbed carbon and gaseous hydrogen. Pulse experiments displayed this reaction above 350°C; at lower temperatures a fraction of the hydrogen either is chemisorbed or remains attached to the carbon. We have obtained infrared and magnetic evidence (to be published) which indicates complete dissociation of methane also below 175°C. This was also found by Galwey (*13*).

One of the most important results is the fact that reaction of the deposited carbon with hydrogen leads to methane only. Rabo and co-workers (*8*) have found that carbon deposited by disproportionation of carbon monoxide reacts at temperatures below 200°C also to higher hydrocarbons (C_2 to C_5). We feel that this difference might have important implications for the mechanism of the Fischer–Tropsch reaction. The difference may be due to the fact that carbon atoms resulting from the decomposition of methane are deposited at longer mutual distances from one another than carbon atoms from carbon monoxide. The large drop in reactivity of the deposited carbon by keeping the catalyst at temperatures above 350°C was also observed by Rabo *et al.* (*8*). It agrees with the slow conversion of chemisorbed carbon atoms and amorphous carbon into more stable graphite at temperatures above 600 K, as was reported by McCarty and Wise (*9*).

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