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Chemisorption of Methane on Ni/SiO$_2$ Catalysts and Reactivity of the Chemisorption Products toward Hydrogen

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The chemisorption of hydrogen both on bare and carburized Ni/SiO$_2$ catalysts was studied using a low-field magnetic method, infrared spectroscopy, and mass spectrometry. With a freshly reduced and evacuated sample of one of the catalysts, H$_2$ chemisorption was investigated as a function of the temperature ($30 < T < 100$°C). It was found that the slope of the magnetization-volume isotherm decreased with increasing temperature, which does not agree with the theory of superparamagnetism. The smaller slope at more elevated temperatures was ascribed to a more extensive coverage of the smaller nickel particles after admission of the initial H$_2$ doses. Carburization of the catalysts was established by the decomposition of CH$_4$ at temperatures from 30 to 300°C. At low surface coverages the carbon was deposited as Ni$_3$C strongly affecting the magnetization. At higher surface coverages CH$_x$-complexes without any effect on the magnetization were chemisorbed. After the decomposition of CH$_4$ the catalysts were evacuated at 250°C, which was found to result in the conversion of a part of the carbonaceous deposit into methane. Also with the subsequent chemisorption of hydrogen on the carburized catalysts (T = 30°C) the reaction between chemisorbed H-atoms and deposited carbon was apparent from the production of CH$_4$. From a comparison of the magnetization-volume isotherms for H$_2$ chemisorption before and after the deposition of small amounts of carbon it was derived that the decomposition of methane preferentially proceeds on small nickel crystallites. Finally it was found that hydrogen was adsorbed not only on bare nickel (with magnetic effect) but also on nickel carbide (without magnetic effect).

INTRODUCTION

In earlier work (*1*, *2*) we reported on the interaction of methane with nickel-on-silica catalysts at temperatures from 30 to 350°C. It was established that methane reacted according to $CH_4 \rightarrow C(ads) + 4H(ads)$. At more elevated temperatures hydrogen desorbed. Low-field magnetic measurements showed that Ni$_3$C and Ni–H were formed up to a surface coverage of 0.8. Beyond coverages of 0.8 methane was chemisorbed without any effect on the magnetization.

The first of the above papers also dealt with the reaction of the deposited carbon with a flow of hydrogen. Reaction was apparent from gaseous reaction products detected gas chromatographically. From 30 to 450°C the deposited carbon was observed to react exothermally to methane; above 300°C the reactivity sharply dropped. In this paper the interaction of gaseous hydrogen with nickel-on-silica catalysts having decomposed known amounts of methane is studied in more detail. To that end the extent of hydrogen chemisorption on carburized samples has been measured volumetrically.

The interpretation of the results of the volumetric measurements, however, appeared to be difficult. After exposure to CH$_4$ the nickel surface is covered by carbon and hydrogen atoms. Subsequent evacuation at 250°C prior to hydrogen chemisorption leads to the desorption both of hydrogen and of methane. As a result the amounts of C(ads), CH$_x$(ads), and H(ads) present before the admission of hydrogen

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are not accurately known. To meet this problem three techniques have been applied. To establish whether CH_x $(1 < x < 4)$ surface species were present prior to or after the admission of H_2 to a carburized catalyst sample infrared spectroscopy was used: this is a suitable technique to detect the presence of a C–H bond, the hydrogen atom of which is not strongly interacting with other atoms. Low-field magnetic measurements proved to be very useful to establish the extent of reaction to gaseous CH_4 during evacuation (after CH_4 chemisorption) and subsequent hydrogen adsorption. Finally, the composition of the gas phase could be monitored by means of a high-frequency mass spectrometer.

Previously we obtained evidence that at low temperatures small nickel particles react more extensively with methane than large particles. To confirm the effect of the size of the nickel particles we used two different types of Ni/SiO_2 catalysts, namely, one containing Ni particles of diameters up to about 150 Å and one with particles of diameters up to 80 Å. Moreover, the preparation method was varied.

EXPERIMENTAL

The catalysts were prepared by precipitation of Ni(II) ions from an aqueous solution onto suspended silica (Aerosil, Degussa). Precipitation was effected by means of urea decomposition at 90°C (catalysts denoted by U), or by injection of hydroxyl ions at 90 or 25°C (catalysts denoted by I). Both preparation procedures were dealt with in detail by Hermans and Geus (*3*) and Van Dillen *et al.* (*4*). The pretreatment and the characterization of the catalysts were described before (*2*); Table 1 summarizes some of their characteristics.

Evacuation and subsequent adsorption experiments were performed in a Pyrex high-vacuum system (*2*). Hydrogen admitted to the catalyst sample (weight about 2 g) was purified by diffusion through palladium. During the adsorption measurements the magnetization of the catalyst was measured in a low-field "permeameter," technical data of which have been given by Erkelens and Wösten (*5*); the alternating (260 Hz) field strength was 66 Oe (1 Oe = 79.58 Am^{-1}).

The measurements on the chemisorption of CH_4 were also performed in this equipment. The procedures applied have been extensively described previously (*2*). Analysis of the gas phase was carried out by means of a high-frequency mass spectrometer (Leybold Heraeus, Topatron B).

Prior to the adsorption experiments the catalysts were verified to be superparamagnetic. To that end the magnetization of the freshly reduced and degassed catalysts was plotted as a function of H/T (H = magnetic field strength, T = absolute temperature). A straight line, indicating superparamagnetic behavior, was obtained for all catalysts in the entire temperature range from 124 to 392 K (*2*). The magnetization was always measured within this range.

TABLE 1

Some Characteristics of the Catalysts Used

Catalyst code	Surface area of aerosil (m^2 g^{-1})	Temperature of preparation (°C)	Wt% Ni in the precipitate	Reduction temperature (°C)	Degree of reduction (%)	Surface area of Ni (m^2 g^{-1} Ni)
I_{42}(25)	380	25	50	470	86	81
I_{42}(90)	380	90	50	550	99	79
U_{20}	200	90	10	470	99	177
U_{42}	380	90	50	450	70	90
U_{42}(ir)	380	90	40	450	70	—

The infrared spectra were obtained in the apparatus described by De Jong *et al.* (*6*). The spectra of the catalyst discs (thickness about 0.1 mm) were recorded at room temperature with a Perkin-Elmer 580 B infrared spectrophotometer.

Catalyst U_{42} was used in isothermal experiments. Methane was chemisorbed at 30, 77, or 100°C. The effect on the magnetization was compared with the effect of H_2 chemisorption, also at 30, 77, and 100°C. Information about the reversibility of the CH_4 decomposition was obtained by measuring the change in the magnetization during evacuation at 250°C. Next, hydrogen was adsorbed at 30°C. The nature of the resulting surface species was determined by means of infrared spectroscopy and magnetic measurements. The slope of the magnetization-volume isotherm measured during admission of H_2 at 30°C to the carbon-covered catalyst yields information on the reversibility of CH_4 decomposition as well as on the (already mentioned) preferential chemisorption of CH_4 on the smaller particles.

Using catalysts $I_{42}(25)$, $I_{42}(90)$, and U_{20} the chemisorption of methane was studied nonisothermally in a temperature range from 30 to 300°C. CH_4 was admitted to the catalyst kept at −70°C in a dose that was just sufficient to lead to a monolayer coverage provided the admitted CH_4 completely reacted to Ni_3C and 4Ni–H. The temperature was subsequently raised stepwise. At each temperature (T_x) the amount of CH_4 chemisorbed was calculated after the composition of the gas phase had been established by means of the mass spectrometer. As the magnetization of superparamagnetic Ni particles strongly depends on the temperature, the magnetization was always measured at 30°C. Accordingly, the catalyst being equilibrated at T_x was cooled to 30°C at which temperature the pressure and the composition of the gas phase as well as the magnetization were determined. Subsequently the catalyst was brought to the next temperature. After equilibration at the final temperature (300°C) two additional doses of methane were admitted. With these doses the procedure to determine the pressure and the composition of the gas phase as well as the magnetization of the catalyst was the same as above.

RESULTS

Isothermal Experiments

Infrared spectroscopy. A small amount of catalyst U_{42} was pressed into a disc. No CH_x absorption bands were observed in the infrared spectrum after exposure of the freshly reduced and evacuated catalyst to 51 Torr of CH_4 at 95°C (*2*). After evacuation, 61 Torr of hydrogen was admitted at room temperature; again no CH_x absorption bands were observed. As compared to the spectrum obtained after CH_4 exposure the only difference was a somewhat enhanced transmittance. Also after the catalyst had been subsequently kept at 70°C in the hydrogen atmosphere for 1.5 hr CH_x absorption bands did not appear. Because of the poor transparency of catalyst U_{42} the experiment was repeated with catalyst U_{42} (ir), for which the Ni/SiO_2 ratio is smaller. Neither exposure to 196 Torr of CH_4 at 100°C and a following evacuation at 250°C, nor subsequent admission of 67 Torr of hydrogen at 110°C resulted in the appearance of CH_x absorption bands in the infrared spectrum. Infrared spectroscopy therefore shows that irrespective of the experimental conditions no C–H bonds were present on the nickel surface with a marked component of their bond direction perpendicular to the surface.

Magnetic measurements. In a preceding paper (*2*) the distribution of CH_4 molecules over the differently sized particles of catalyst U_{42} was found to be independent of the temperature ($30 < T < 100$°C). To establish the effect of the temperature on the distribution of H_2 over the same catalyst particles, the magnetization-volume isotherm for H_2 chemisorption was measured at 30, 77, and 100°C. At 30°C the adsorption pro-

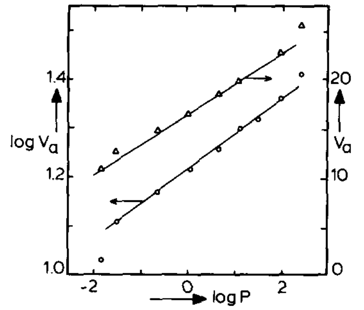

FIG. 1. Freundlich isotherm (○) and Temkin isotherm (△) for the adsorption of H_2 on catalyst U_{42} at 30°C.

ceeded rapidly: at low coverages ($\theta_H < 0.6$) equilibrium was attained within 5 min after the admission of H_2 ($\theta_H = 1$ is defined as the surface coverage attained at a final hydrogen pressure of about 300 Torr). At higher coverages equilibrium was established much more slowly. For values of θ_H above 0.8 equilibrium was not attained within 1.5 hr.

In a large pressure range, 10^{-2} to 10^{+2} Torr, a plot of V_a versus log P_{H_2} (Temkin) as well as a plot of log V_a versus log P_{H_2} (Freundlich) yielded a straight line (Fig. 1). A plot of $P_{H_2}^{1/2}/V_a$ versus $P_{H_2}^{1/2}$ (Langmuir) showed a linear relation in a more limited pressure range, 0.5–30 Torr. At 77 and 100°C the rate of hydrogen adsorption was fast even at high surface coverages. In Fig. 2 the three magnetization-volume isotherms are represented; M is the actual magnetization and M_0 is the magnetization when $V_a = 0$. It can be seen that the initial slope of the isotherm decreases with increasing temperature.

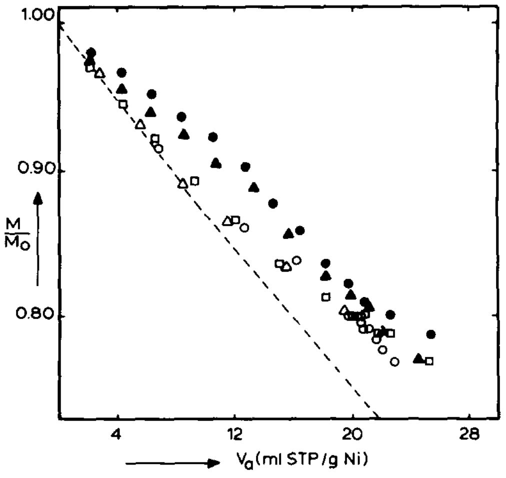

FIG. 2. Relative magnetization of catalyst U_{42} as a function of the amount of H_2 adsorbed. △, □, ○, T = 30°C; ▲, T = 77°C; ●, T = 100°C.

The slope of the magnetization-volume isotherm for the decomposition of CH_4 was observed to be independent of the temperature (*2*). At all temperatures the decomposition was reported to proceed according to $CH_4 + 7Ni \rightarrow Ni_3C$ (surface nickel carbide) + 4Ni–H. The chemisorption of methane appeared to be an activated process: the amount of CH_4 taken up at a fixed exposure was larger at higher temperatures. The activation energy was previously (*1*) reported to be 6 kcal mole^{-1}. When after the chemisorption of methane the catalyst was evacuated at 250°C for 5 hr, the magnetization of the sample considerably increased. After chemisorption at 30°C of 2.6×10^{-2} ml STP m^{-2} Ni of CH_4 the relative magnetization dropped to 93%. Subsequent evacuation raised the relative magnetization by about 5.5 to 98.5%. The decrease in M/M_0 by 7% owing to the chemisorption of CH_4 can be divided into two parts:

formation of Ni_3C: $3/7 \times 7\% = 3\%$

adsorption of H-atoms: $4/7 \times 7\% = 4\%$

When during evacuation all hydrogen desorbs, the increase in M/M_0 can be 4% at most. The actual increase was 5.5%. Obviously, also Ni_3C was partly removed according to $Ni_3C + 4H(ads) \rightarrow 3Ni + CH_4(g)$. The amount of CH_4 thus produced was 50% of the originally deposited amount. Similar results were obtained on evacuation at 250°C after CH_4 chemisorption at 77 and 100°C. After the decomposition of 6×10^{-2} ml STP m^{-2} Ni (77°C) and 9×10^{-2} ml STP m^{-2} Ni (100°C) of methane, the extent of the conversion of Ni_3C to CH_4 was also about 50%.

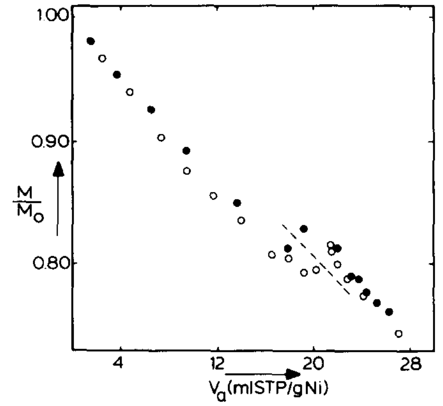

FIG. 3. Relative magnetization of catalyst U_{42} as a function of the amount of H_2 adsorbed at 30°C after carburization at 100°C and subsequent evacuation at 250°C.

During hydrogen adsorption at 30°C on a carburized and evacuated catalyst sample the above conversion of Ni_3C into CH_4 can also proceed. Reaction to CH_4 will affect the slope of the magnetization-volume isotherm: owing to the reaction a pressure drop is observed (two H_2 molecules are required to produce one CH_4 molecule), which will be erroneously interpreted as an increase in the extent of hydrogen adsorption (no partial pressures were recorded in the measurements). Moreover, the regeneration of metallic Ni from Ni_3C will lead to an increase in magnetization. As a result, an apparent increase in V_{H_2} is accompanied by an increase in the magnetization. This effect, superimposed on the decrease in magnetization during H_2 chemisorption, will lead to a smaller slope of the magnetization-volume isotherm. In Fig. 3 the magnetization-volume isotherm for H_2 chemisorption on a catalyst sample which had been previously carburized at 100°C and evacuated at 250°C is shown. The isotherm was measured twice; in each isotherm a discontinuity exists where the interval between successive hydrogen doses was larger than the usual, viz. 16 hr as against 1.5 hr. During that period the pressure in the sample cell decreased, whereas the magnetization of the sample rose. From the apparent increase of V_{H_2} and of the magnetization it can readily be seen that at 30°C the rate of the surface reaction between Ni_3C and H(ads) is very small. Consequently the initial slope of the magnetization-volume isotherm will only slightly differ from the one measured with the bare nickel surface. This is illustrated in Fig. 4. After interaction with CH_4 at 100°C and evacuation at 250°C the carbon surface coverage was about 2.9×10^{-2} ml STP m^{-2} Ni. The initial slope of the H_2 isotherm subsequently measured is almost the same as on the clean surface. After carburization at 30 or 77°C, where the residual carbon coverage was about 1.3×10^{-2} and 2.2×10^{-2} ml STP m^{-2} Ni, the slope of the H_2 isotherm has even become larger. As will be discussed later, the larger initial slope is related to the preferential decomposition of methane on the smallest nickel particles.

Nonisothermal Measurements

Using catalysts U_{20}, $I_{42}(90)$, and $I_{42}(25)$ the decomposition of methane was also studied nonisothermally in a temperature range from 30 to 350°C. A freshly reduced and evacuated catalyst sample was exposed at 30°C to a methane dose. To prevent tran-

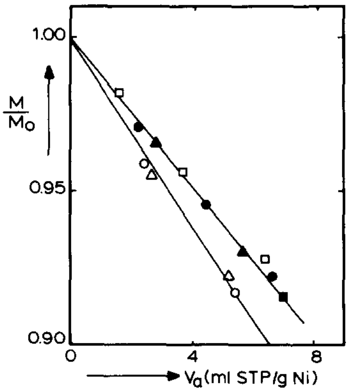

FIG. 4. The initial slope of the magnetization-volume isotherm for the adsorption of H_2 on catalyst U_{42} at 30°C. ●, ■, ▲, Bare nickel; ○, after carburization at 30°C and evacuation at 250°C; △, after carburization at 77°C and evacuation at 250°C; □, after carburization at 100°C and evacuation at 250°C.

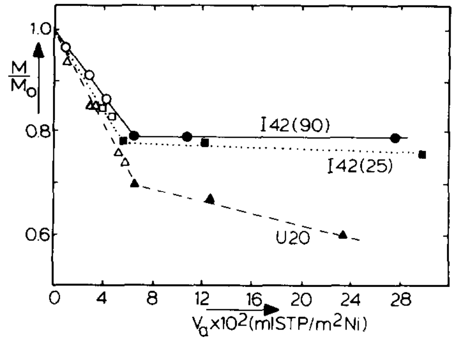

FIG. 5. The relative magnetization of catalysts U_{20}, $I_{42}(90)$, and $I_{42}(25)$ as a function of the amount of methane adsorbed. △, □, ○, Adsorption during a temperature rise from 30 to 300°C; ▲, ■, ●, adsorption at 300°C.

sient heat effects the methane was admitted at −70°C. Provided each CH_4 molecule is bonded to seven Ni surface atoms, the dose was sufficient to lead to a monolayer coverage. Next the temperature was raised stepwise up to 300°C. At several intermediate temperatures the amount of CH_4 taken up after equilibration was determined. For all catalysts it was observed that above 150°C H_2 started to desorb from the catalyst surface. Because the magnetization was always measured after cooling to 30°C, the amount of methane taken up, V_a, was established also at 30°C after determination of the P_{CH_4}/P_{H_2} ratio by means of the mass spectrometer. Figure 5 shows the results; those for catalysts $I_{42}(90)$ and U_{20} have already been published (2). For all catalysts the magnetization decreased linearly with V_a. However, additional adsorption of methane at 300°C no longer brought about a decrease in magnetization with catalysts $I_{42}(25)$ and $I_{42}(90)$; the magnetization of catalyst U_{20}, on the other hand, continued to decrease, though exhibiting a much smaller slope.

For the points measured at 300°C, indicated by filled symbols in Fig. 5, the surface coverages of carbon and hydrogen, as obtained after cooling from 300 to 30°C, are given in Table 2. It can be seen that with catalyst $I_{42}(25)$ almost all hydrogen evolved readsorbed upon cooling, resulting in a H/C surface ratio of nearly four. Furthermore it is clear that on all catalysts at the last measuring point the extent of carbon chemisorption surpasses the monolayer capacity of Ni_3C (a monolayer would correspond to about 0.19 ml STP "C" m^{-2} Ni). Finally it is striking that also the amount of hydrogen eventually taken up exceeds the monolayer capacity of about 0.28 ml STP H_2 m^{-2} Ni, despite the presence of a large amount of carbon at the surface.

In Fig. 6 the decrease in magnetization of catalyst U_{20} due to the decomposition of CH_4 is compared with the magnetic effect of hydrogen chemisorption on the bare and carbon-covered catalyst at 30°C. During CH_4 decomposition the relative magnetization dropped to a level that was also attained when a monolayer of hydrogen was chemisorbed (final H_2 pressure about 300 Torr). The slope of the curve was, however, much smaller after uptake of 0.06 ml STP m^{-2} Ni. Subsequent evacuation at 250°C caused the relative magnetization to rise considerably, from 0.61 to 0.88. In a calculation, similar to that made above for catalyst U_{42}, it is readily derived that at least 29% of the originally deposited carbon desorbs as CH_4 from the surface during the evacuation. The results of hydrogen chemisorption at 30°C on the carburized and evacuated catalyst U_{20} are also represented

TABLE 2

The Amounts of Carbon and Hydrogen Adsorbed at 30°C on Catalysts U_{20}, $I_{42}(90)$, and $I_{42}(25)$ after CH_4 Chemisorption at 300°C

Catalyst	Amount of carbon adsorbed (ml STP "C" m^{-2} Ni)	Amount of hydrogen adsorbed (ml STP H_2 m^{-2} Ni)	H/C ratio on the surface
U_{20}	0.066	0.113	3.4
	0.126	0.195	3.1
	0.235	0.325	2.8
$I_{42}(90)$	0.062	0.100	3.2
	0.108	0.129	2.4
	0.274	0.360	2.6
$I_{42}(25)$	0.056	0.109	3.9
	0.122	0.169	2.8
	0.301	0.411	2.7

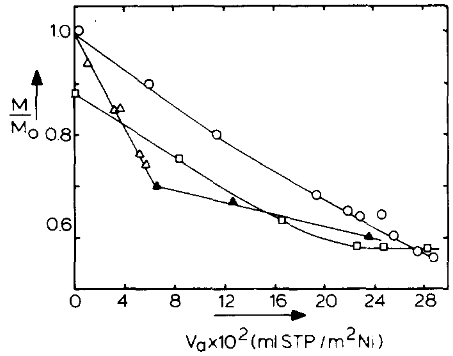

FIG. 6. The relative magnetization of catalyst U_{20} as a function of the amount of CH_4, or H_2, adsorbed. △, Chemisorption of CH_4 during a temperature rise from 30 to 300°C; ▲, subsequent chemisorption of CH_4 at 300°C; ○, chemisorption of H_2 at 30°C on the bare catalyst; □, chemisorption of H_2 at 30°C after CH_4 chemisorption and subsequent evacuation at 250°C.

in Fig. 6. The initial slope of the hydrogen isotherm is very much the same as on clean nickel. The main difference is that at surface coverages above about 0.20 ml STP H_2 m^{-2} Ni the magnetization no longer decreases upon further adsorption. The final relative magnetization attained is about the same as with H_2 adsorption on bare nickel.

In Fig. 7 the results obtained with catalyst $I_{42}(90)$ are represented. In several aspects this catalyst behaved differently as compared to catalyst U_{20}:

(a) During the decomposition of CH_4 the magnetization did not drop as far as was observed during the chemisorption of H_2, whereas on catalyst U_{20} eventually the same level was attained.

(b) The rise of the magnetization (ΔM) from 0.76 to 0.85 during evacuation at 250°C was much smaller than with catalyst U_{20} (0.61 to 0.88). Actually ΔM was so small that it can be derived that only part of the hydrogen desorbed from the surface during evacuation.

(c) The initial slope of the H_2 isotherm after carburization (s_a) was less steep than that measured on bare nickel (s_b): $s_a/s_b = 0.8$. At saturation the decrease in magnetization was equal to that measured after hydrogen adsorption on the bare Ni surface. As we argued above, the smaller initial slope can be ascribed to the conversion of chemisorbed carbon into $CH_4(g)$. Whereas the rate of this reaction was slow on catalyst U_{42}, the larger surface coverage of carbon remaining after evacuation may have raised the reaction rate on catalyst $I_{42}(90)$. The increased production of CH_4 was also confirmed by means of the mass spectrometer. At a final H_2 pressure of 206 Torr an amount of CH_4 of 0.5×10^{-2} ml STP m^{-2} Ni was detected in the gas phase. Additionally the slope of the magnetization-volume isotherm may have been smaller because of simultaneous adsorption of hydrogen both on Ni_3C and on ferromagnetic Ni from the first H_2 dose on. With catalysts U_{42} and U_{20}, containing less Ni_3C after evacuation, the hydrogen initially admitted is taken up mainly by ferromagnetic nickel.

Catalyst $I_{42}(25)$ showed a behavior analogous to that of catalyst $I_{42}(90)$. During CH_4 decomposition (Fig. 5) the relative magnetization did not drop below 0.77, whereas after H_2 chemisorption a much lower value, viz. 0.65, was attained. Evacuation at 250°C caused the relative magnetization to rise from 0.77 only to 0.82. The ratio s_a/s_b of the initial slopes of the hydrogen isotherms (see above) was much smaller than with

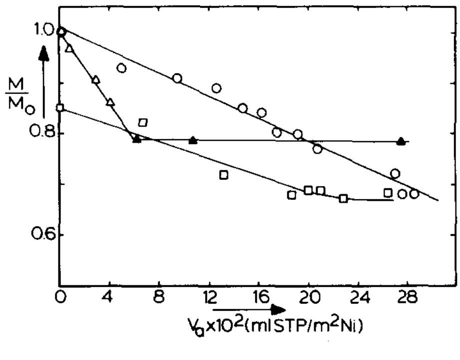

FIG. 7. The relative magnetization of catalyst $I_{42}(90)$ as a function of the amount of CH_4, or H_2, adsorbed. △, Chemisorption of CH_4 during a temperature rise from 30 to 300°C; ▲, subsequent chemisorption of CH_4 at 300°C; ○, chemisorption of H_2 at 30°C on the bare catalyst; □, chemisorption of H_2 at 30°C after CH_4 chemisorption and subsequent evacuation at 250°C.

catalyst $I_{42}(90)$: $s_a/s_b = 0.6$. This low value indicates an enhanced rate of CH_4 production. At a final H_2 pressure of 220 Torr the amount of CH_4 in the gas phase was 1.2×10^{-2} ml STP m^{-2} Ni.

DISCUSSION

Distribution of Admitted Hydrogen Molecules over the Nickel Particles

We first will deal with the distribution of the admitted gas molecules over the differently sized nickel particles present in the catalysts. Previously (*2*) the slope of the magnetization-volume isotherm for the chemisorption of CH_4 on catalyst U_{42} was reported to be unaffected by the temperature ($30 < T < 100°C$). In Fig. 2 it is shown that the slope of the H_2 isotherm decreases with increasing temperature. According to the low-field theory of superparamagnetism the decrease of the magnetization which is due to the adsorption of hydrogen at 30°C can be described for a monodisperse system by the following equation (*7*):

$$\frac{M}{M_0} = 1 - 1.31 \times 10^{-2} V_a + 4.31 \times 10^{-5} V_a^2$$

$$V_a = \text{ml STP } H_2 \text{ g}^{-1} \text{ Ni}.$$

This "theoretical" curve is indicated in Fig. 2 by the dashed line. It can be seen that the hydrogen isotherm at 30°C initially fits well the theoretical curve. When V_a exceeds 10 ml STP g^{-1} Ni the experimental isotherm deviates from the dashed line. This can be ascribed to the nonuniform particle size of the nickel crystallites in the catalyst: Reinen and Selwood (*8*) have shown that for samples containing a distribution of particle sizes the decrease of the magnetization may become smaller than expected from the above equation. The spontaneous magnetization, M_{sp}, is lower at higher temperatures (*7*). The initial slope of the magnetization-volume isotherm, which is inversely proportional to M_{sp}, is therefore expected to be larger at more elevated temperatures. As can be seen, however, in Fig. 2 the initial slope of the isotherm decreased as the temperature rose. It has been pointed out previously (*2*) that preferential adsorption on the larger particles of a given size distribution causes the initial slope to be larger than preferential adsorption on the smaller crystallites does. Hence it is concluded that at 30°C the hydrogen is adsorbed mainly on the larger particles. The smallest crystallites in the narrowest pores of the catalyst are only partly reached. When the temperature increases, the equilibrium constant for the equilibrium $H_2(g) \rightleftarrows 2H(ads)$ drops. Moreover, the time of adsorption, τ, of a hydrogen atom on the nickel surface decreases (*9*). The transport of hydrogen through the pores of the catalyst is consequently facilitated and initially the smallest crystallites are more extensively covered. Hence the initial slope of the isotherm decreases.

Preferential Adsorption of CH_4 on Smaller Ni Particles

Whereas with H_2 chemisorption the smaller particles of catalyst U_{42} are more difficult to reach, the chemisorption of CH_4 displaying a much smaller sticking probability has been reported (*2*) to proceed preferentially on these particles. This was derived from the larger amount of CH_4 taken up per unit surface area at 30°C by the highly dispersed catalyst U_{20} (1.05×10^{-2} ml STP m^{-2} Ni) as compared to catalyst $I_{42}(90)$ (0.16×10^{-2} ml STP m^{-2} Ni). Preferential adsorption of CH_4 on the smaller particles is also apparent from the experimental results of this paper. After isothermal chemisorption at 30 or 77°C on catalyst U_{42} and subsequent evacuation at 250°C, the initial slope of the H_2 isotherm is larger than on the bare nickel catalyst. Because during evacuation of the carbided catalyst U_{42} a large fraction of the deposited carbon reacted to CH_4 (see previous section), the carbon surface coverage was small when hydrogen was admitted. Consequently, the rate of the reaction $Ni_3C + 4Ni\text{-}H \rightarrow CH_4 + 7Ni$ will have been small. The larger initial slope of the H_2 isotherm can then be explained only by assuming that for a fixed value of $V(H_2)$ the adsorption on the larger particles is more extensive with the carbided catalyst than with the clean catalyst. Hence, the chemisorption at 30°C on the smaller Ni particles, which, as argued above, is already suppressed with the bare catalyst, is still further diminished. The further drop in the extent of H_2 chemisorption on the smaller Ni-crystallites of the carbided catalyst is to be ascribed to the presence of carbon atoms which apparently are deposited preferentially on these particles and/or are the most stable during evacuation. When after evacuation the surface concentration of carbon is larger, i.e., after CH_4 chemisorption at 100°C on catalyst U_{42} or after nonisothermal carbon deposition on catalysts U_{20}, $I_{42}(90)$, and $I_{42}(25)$, the slope of the H_2 isotherm decreases again because of the reaction: $Ni_3C + 4Ni\text{-}H \rightarrow CH_4 + 7Ni$. Preferential chemisorption of methane on small nickel particles has also been reported by Martin *et al.* (*10*). The conclusion of these authors was based on a comparison of magnetic effects during CH_4 chemisorption at low and high magnetic fields.

Incomplete Dissociation of Methane

Our observations about the preferential chemisorption of CH_4 on the smaller nickel particles are in agreement with the results of Schouten *et al.* (*11, 12*), who found that the decomposition of methane on nickel single crystals depended on the atomic structure of the crystallographic plane: on Ni(110) methane was readily decomposed above 200°C and at pressures up to 10^{-2} Torr, whereas the reaction was much slower on Ni(100). On Ni(111) no methane at all was decomposed. The selectivity of the CH_4 decomposition, proceeding at an enhanced rate on atomically rough crystallographic planes, also explains that at surface coverages above about 6×10^{-2} ml STP CH_4 m^{-2} Ni the chemisorption of CH_4 no longer proceeds according to $CH_4 + 7Ni \rightarrow Ni_3C + 4Ni\text{–}H$ (Fig. 5). With catalysts U_{42}, $I_{42}(90)$, and $I_{42}(25)$ further adsorption is not accompanied by a drop in the magnetization, whereas with catalyst U_{20} the rate of the decrease is strongly diminished. Apparently, at more elevated surface coverages the formation of Ni_3C is inhibited.

At high coverages methane is still chemisorbed with the release of hydrogen as can be concluded from the decrease in the H/C surface ratios in Table 2. For some reason, however, the penetration of carbon into the Ni surface is impeded. Moreover, it is striking that the magnetization is not further decreased by the hydrogen released down to the level observed during H_2 chemisorption on the bare Ni catalyst. We feel that the chemisorption of methane after completion of the fully dissociative chemisorption on atomically rough crystallographic planes proceeds on more closely packed planes according to $CH_4 \rightarrow CH_x + (4 - x)H$, $1 \leq x < 4$. Accordingly carbon–hydrogen complexes CH, CH_2, or CH_3 are being chemisorbed without affecting the ferromagnetism. These complexes are covering the Ni surface, thus preventing that the hydrogen set free at 300°C is readsorbed (with magnetic effect) on cooling to 30°C, at which temperature the magnetization was measured. Because the carbon atom is still bonded to hydrogen atoms it cannot penetrate into the nickel surface to form Ni_3C and consequently there is no decrease in the magnetization. The presence of CH_x-species explains why even in the presence of large amounts of carbon at the surface, the amount of hydrogen taken up exceeds the monolayer coverage (Table 2). With the highly dispersed catalyst U_{20} the magnetization continued to drop, though much more slowly, at surface coverages above 6×10^{-2} ml STP CH_4 m^{-2} Ni. On the small particles of this catalyst apparently part of the CH_x-complexes dissociates at a low rate to Ni_3C and adsorbed hydrogen, and this brings about the gradual decrease of the magnetization.

The infrared experiments described in this paper were not appropriate to study the nature of the CH_x-complexes at high surface coverage. With the exposures used we are not sure that the surface coverage attained was larger than 6×10^{-2} ml STP CH_4 m^{-2} Ni (no simultaneous volumetric measurements could be carried out). Hence, the absence of C–H absorption bands may be due to the fact that $V(CH_4)$ was still so small that all methane taken up was chemisorbed according to $7Ni + CH_4 \rightarrow Ni_3C + 4Ni\text{–}H$, without the formation of CH_x-species. Infrared spectroscopic measurements after more prolonged exposures to CH_4 at more elevated temperatures will be the subject of future research.

Evacuation of the carburized catalysts brought about the removal from the surface of the adsorbed CH_x-complexes, as can be concluded from the large extent of the subsequent hydrogen adsorption (Figs. 6 and 7). Apparently, adsorbed hydrogen atoms recombine with the surface complexes during evacuation to yield CH_4. This can be explained by the slow transport of H_2 out of the catalyst pores during evacuation. Hydrogen to be pumped off is readsorbed frequently on the catalyst surface before it leaves the catalyst bed. For CH_4, which is chemisorbed in an activated process and hence exhibits a smaller sticking probability, this effect is far less pronounced. As a result the equilibrium $CH_4 \rightleftarrows CH_x(ads) + (4 - x)H(ads)$ is shifted to the left side. On this line of argument the magnetization can be increased at most by a fraction corresponding with the desorption of all hydrogen atoms from the surface, for the CH_x-species were chemisorbed without magnetic effect. However, with catalysts U_{20} and U_{42} it was observed that the rise of the magnetization during evacuation was larger than the increase expected for a complete desorption of the chemisorbed hydrogen. As argued above, 29% of the Ni_3C of catalyst U_{20} reacted to CH_4, and of catalyst U_{42} about 50%. The disappearance of the Ni_3C accounts for the additional magnetic effect.

With catalysts $I_{42}(25)$ and $I_{42}(90)$, on the other hand, the increase in magnetization during evacuation was smaller than corresponds to complete hydrogen desorption. In our opinion another mechanism was operative here. Because the evacuation procedure for these catalysts (5 hr at 250°C) was the same as that used with the other catalysts, there is no reason to assume that the extent of hydrogen desorption was appreciably smaller. We feel that, because apparently during evacuation not all CH_x-complexes recombined with H(ads) to CH_4, the remaining CH_x-species dissociated to Ni_3C and gaseous hydrogen, thus additionally lowering the magnetization. This explanation also accounts for the small initial slope of the subsequently measured magnetization-volume isotherm for H_2 chemisorption. The ratio of slopes, s_a/s_b (see above), was smaller for the catalysts $I_{42}(90)$ ($s_a/s_b = 0.8$) and $I_{42}(25)$ ($s_a/s_b = 0.6$) than for catalyst U_{20} ($s_a/s_b > 0.9$). The smaller initial slope is due (as already discussed) to the reaction $Ni_3C + 4H\text{-}Ni \rightarrow CH_4 + 7Ni$, which proceeds simultaneously with the measurement of the H_2 isotherm. Obviously, the rate of this reaction was enhanced on catalysts $I_{42}(90)$ and $I_{42}(25)$ owing to the larger carbon surface coverage remaining after evacuation.

Finally it should be noted that at large surface coverages hydrogen was adsorbed on the carburized and evacuated samples without magnetic effect (Figs. 6 and 7). This has to be ascribed to adsorption on the remaining nickel carbide. From the infrared measurements it can be derived that the hydrogen was not bonded to the "carbidic" carbon atom without interacting with other surface (nickel) atoms, for no C–H absorption bands were observed in the infrared spectrum. Alternatively, the hydrogen atom is not bonded to the carbon atom at all, but to the already magnetically decoupled nickel atoms. We feel that the observed possibility of hydrogen chemisorption on a surface nickel carbide may have important implications for the mechanism of the methanation reaction. We will report on a study of this reaction in a forthcoming paper.

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