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Carbon Deposition from CH_4 and CO on Ni/SiO_2: Effects on the Nickel Surface Structure

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The activity of supported Ni catalysts for the decomposition of methane was found to be raised by subjecting the catalyst to an increasing number of carburization–decarburization cycles. Carburization was effected either by the decomposition of methane ($CH_4 \rightarrow C(ads) + 2H_2$) or by the disproportionation of carbon monoxide ($2CO \rightarrow C(ads) + CO_2$). Decarburization always was carried out by hydrogen ($C + 2H_2 \rightarrow CH_4$). It was observed that the rise in activity for the decomposition of methane was related to an increased capacity of the catalyst for the chemisorption of hydrogen at 30°C. From the results it was concluded that the surface of the nickel particles is reconstructed in the presence of carbon atoms. After reduction in H_2 at 450°C a very small amount of strongly bound carbon remains in the surface, thus inhibiting the relaxation of the surface to its original state.

INTRODUCTION

In a previous paper (*1*) we reported on the deposition of carbon on a Ni/SiO_2 catalyst by the decomposition of methane, as well as on the reactivity of the deposited carbon toward hydrogen. In subsequent experiments with a larger number of nickel catalysts it was established that the activity for the decomposition of CH_4 gradually increased as a function of the number of "carburization–decarburization" cycles to which the catalyst had been subjected. Because the catalytic activity of a catalyst is determined both by the active surface area per unit weight and by the specific activity per unit surface area, we wondered if the surface of our catalysts changed during the exposure to CH_4 and/or the subsequent carbon removal. We therefore determined the specific nickel surface area of one of the catalysts before and after the catalyst had been submitted to a known number of carburization–decarburization cycles. To that end hydrogen chemisorption experiments were performed at 30°C. Because the nature of the deposited carbon was supposed to be an important variable, carbon was deposited not only by the decomposition of methane but also by the disproportionation of carbon monoxide.

The decomposition of methane was always effected in a flow system by pulsing small doses of CH_4 into a nitrogen flow passing through the reactor kept at 275°C. The disproportionation of carbon monoxide was carried out in a Pyrex high-vacuum system by admitting small doses of CO to the evacuated catalyst at 275°C. Carbon deposited either by CH_4 decomposition or by CO disproportionation was removed from the surface in a hydrogen flow at temperatures up to 450°C. After carbon removal the catalyst was evacuated at 425°C and the extent of hydrogen chemisorption was measured. The value then found was compared with the hydrogen volume chemisorbed on a sample that had not been exposed to CH_4 or CO previously.

EXPERIMENTAL

In the present investigation four different nickel catalysts have been used. Two nickel-on-silica catalysts, U_{42} and U_{46}, were

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prepared by the method of homogeneous deposition–precipitation by means of urea decomposition at 90°C, as described by Hermans and Geus (*2*) and van Dillen *et al.* (*3*). The silica used was Aerosil (Degussa, 380 m^2 g^{-1}). The precipitate of catalyst U_{42} contained 50 wt% Ni, whereas the weight content of Ni in catalyst U_{46} was only 11%. Two other catalysts, G_{33} and G_{65}, were obtained from Girdler. According to the specifications the Ni content of catalyst G_{33} reduced at 500°C was 30 wt%, while that of catalyst G_{65} was 25 wt%. The support of catalyst G_{33} contained $Al_2Si_2O_5(OH)_4$, $CaCO_3$ and SiO_2; catalyst G_{65} had an alumina support to which "alkali" (8 wt%) and graphitic carbon (4 wt%) had been added. All catalysts were dehydrated in N_2 at 450°C, subsequently reduced in 10% H_2/90% N_2 at the same temperature (unless indicated otherwise) for at least 80 h, and finally degassed in a N_2 flow at 450°C for 2 h.

The equipment used in the experiments on the decomposition of methane was the same as described before (*1*). Nitrogen was deoxygenated by BASF catalyst R-3-11 (BTS catalyst), and dehydrated by Linde molecular sieve, Type 4A; hydrogen was deoxygenated by a Baker "deoxo"-catalyst (Pd/alumina). A mixture of 10.2% CH_4 and 89.8% N_2 (impurities less than 70 ppm) was supplied by Matheson.

The measurements were performed with small catalyst beds (length about 1.5 cm and diameter 2 cm); the size of the catalyst pellets varied between 1.5 and 2.5 mm. The procedure during a typical carburization–decarburization experiment was as follows. A dose of 0.15 ml STP of methane was pulsed into nitrogen flowing through the reactor kept at the desired temperature T_1 ($T_1 \leq 350°C$). The CH_4 conversion was determined gas chromatographically. The carbonaceous deposit was removed with H_2 pulses, initially also at T_1 and subsequently at temperatures increasing from T_1 to 450°C. Finally the catalyst sample was rereduced at 450°C in a flow of 10% H_2 and 90% N_2 for 16 h. Prior to the next carburization–decarburization experiment at T_2 all hydrogen was removed from the catalyst surface by passing a flow of N_2 through the reactor for 2 h at 450°C.

Carbon deposition by means of the Boudouard reaction, $2CO \rightarrow C + CO_2$, was effected at 275°C on catalyst U_{42} only in a conventional Pyrex high-vacuum apparatus (background pressure 10^{-5}–10^{-6} Torr; 1 Torr = 133.3 Nm^{-2}) as described before (*4*). The carbon deposited from CO was removed from the nickel surface in a flow of 10% H_2 and 90% Ar during a gradual temperature rise from 22 to 450°C.

The hydrogen chemisorption experiments were carried out at 30°C in the same high-vacuum apparatus as used for the Boudouard reaction; these experiments also were performed with catalyst U_{42} only. After reduction of the fresh catalyst, or after carbon deposition (either from CH_4 or CO) and subsequent removal (as indicated above), the catalyst was evacuated for at least 5 h. The temperature maintained during evacuation was about 25°C below the reduction temperature to prevent desorption of water from the support and subsequent reoxidation of the nickel metal. Hydrogen used in the adsorption experiments was purified by diffusion through palladium.

The particle size distribution of catalyst U_{42} was obtained by means of a vibrating sample magnetometer (fields up to 14 kOe; 1 Oe = 79.58 A m^{-1}), which also has been described earlier (*4*).

Transmission electron micrographs were made by means of a JEOL 200 C electron microscope. Reduced samples were suspended in methylmethacrylate, which was polymerized at 60°C. Ultrathin sections of these samples, suited for the electron microscope, were cut with a Reichert ultramicrotome.

RESULTS AND DISCUSSION

The decomposition of methane was investigated in pulse-flow experiments with four different catalysts, U_{42}, U_{46}, G_{33}, and G_{65}. As described in the experimental section a dose of 0.15 ml STP of methane was pulsed into a nitrogen flow passing through the reactor and the conversion of CH_4 was measured. Subsequently the carbonaceous deposit was removed by hydrogen pulses at increasing temperatures and finally in a continuous flow of hydrogen at 450°C. It was observed that the CH_4 conversion at a fixed temperature gradually changed as a function of the number of carburization–decarburization cycles to which the catalyst had been subjected.

Some representative results have been collected in Table 1. It can be seen that the CH_4 conversion increased appreciably with the number of cycles. It was established that with the above-mentioned procedure of carbon removal within experimental error all deposited carbon reacted with H_2. Methane appeared to be the only reaction product.

TABLE 1

The Conversion of a CH_4 Pulse at 200°C on Various Catalysts as a Function of the Number of Carburization-Decarburization Cycles Performed

Catalyst	Reduction temperature (°C)	Conversion during first carburization (%)	Conversion during *n*th carburization (%)	
			n	Conversion
U_{42}	450	78	>40	93
U_{46}	450	62	2	79
G_{33}	500	68	5	79
G_{65}	625	44	6	63

To investigate the effect of carbon deposition and subsequent removal on the extent of hydrogen chemisorption, catalyst U_{42} (see Table 1) was passivated in a flow of 1 vol% of O_2 in N_2 and afterward transferred to the sample cell of the static adsorption apparatus. In Fig. 1 the hydrogen isotherm measured at 30°C with the re-reduced and evacuated sample is shown. In Fig. 1 also the H_2 isotherm obtained with a freshly reduced sample of catalyst U_{42} that had not been exposed to CH_4 previously is represented. It is evident that the amount of hydrogen chemisorbed, $V(H_2)$, was strongly enlarged by subjecting the catalyst to more than 40 carburization–decarburization cycles. At a hydrogen pressure of 300 Torr $V(H_2)$ had increased by about 50%, while the CH_4 conversion had increased from 78 to 93% (Table 1).

Reaction with methane and subsequent removal of the carbonaceous deposit with H_2 has also been carried out with the catalyst sample already in the measuring cell of the adsorption apparatus. In this way an intermediate passivation of the sample was prevented. After the sample had been exposed to 270 pulses of 0.15 ml STP of CH_4 at 275°C (four pulses per hour), the deposited carbon was removed in the usual way. As a result of this treatment the extent of hydrogen chemisorption on the sample rose by 13%.

In the adsorption apparatus a sample of catalyst U_{42} was carburized three times by carbon from carbon monoxide according to $2CO \rightarrow C + CO_2$. After each carburization the carbonaceous deposit was removed from the surface by reaction with H_2. Prior to and after the three carburization–decarburization cycles hydrogen was adsorbed on the sample at 30°C. The results are represented in Fig. 2. Again the extent of hydrogen chemisorption increased due to carbon deposition and subsequent removal, now by about 15%.

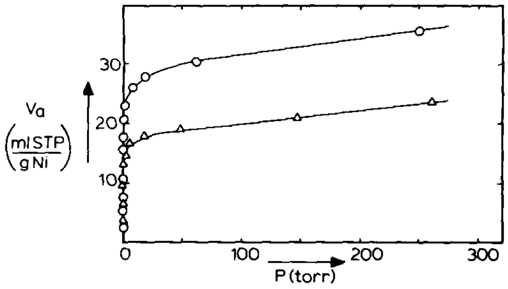

FIG. 1. Isotherms for hydrogen chemisorption at 30°C on a sample of catalyst U_{42} (carburization was effected by means of CH_4 decomposition). (△) Prior to carburization–decarburization experiments, (○) after carburization–decarburization experiments.

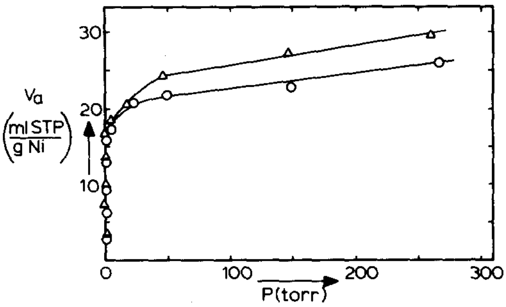

FIG. 2. Isotherms for hydrogen chemisorption at 30°C on a sample of catalyst U_{42} (carburization was effected by means of CO disproportionation). (○) Prior to carburization–decarburization experiments, (△) after carburization–decarburization experiments.

The most obvious inference is to ascribe the increased hydrogen chemisorption to a higher degree of reduction, x, caused by the successive treatments with CH_4 or CO and H_2. We therefore determined the degree of reduction of the sample before and after the experiments of Fig. 2 by measuring the saturation magnetization at 77 K and at a magnetic field strength of 14 kOe. The degree of reduction appeared to have increased only from 71 to 75% in the course of the experiments; this increase in x is too small to lead to a rise in the nickel surface area of about 15%. We also measured the particle size distributions of the sample of Fig. 2. Figure 3 shows the results. In this figure the increment of the nickel volume V in intervals $d(\log r)$ is represented as a function of the radius (r) of the nickel particles. It can be seen that the particle size distribution hardly changed during the experiments. More quantitatively the specific nickel surface area, as calculated from the particle size distribution, decreased by about 15%, probably because of a little sintering during the subsequent reductions (the fresh sample had been reduced at 450°C for 80 h, whereas eventually the sample had been kept at 450°C for 925 h). Hence the increase in $V(H_2)$ by about 15% has to be compared with the decrease in S_{Ni} by about 15% calculated from the magnetically obtained particle size distributions. Apparently, the process of carburization and subsequent decarburization raises the extent of hydrogen chemisorption per unit surface area of nickel.

That also the catalytic activity per unit surface area of nickel was raised by (de-)carburization is demonstrated unambiguously by the following experiment. A sample of catalyst G_{65} was reduced at 450°C and subsequently exposed to a pulse of methane (0.15 ml STP) at 300°C; the conversion measured was 83%. Subsequently the sample was reduced at 625°C. The transmission electron micrographs of Fig. 4 show that during this high-temperature treatment appreciable sintering occurred. As was to be expected, the conversion found (51%) was considerably smaller than before. Obviously the appreciable drop in the nickel surface area evident from Fig. 4 leads to the decreased conversion. After the sample had been (de-)carburized repeatedly, a new measurement of the CH_4 conversion at 300°C yielded a value of 90%. This high conversion was preserved even after another high-temperature reduction at 625°C.

From the above experiments we conclude that the deposition of carbon on the nickel surface, either from CH_4 or CO, leads to a change in the surface structure of the Ni particles. It has been found that within experimental error all carbon was removed from the surface prior to H_2 chemi-

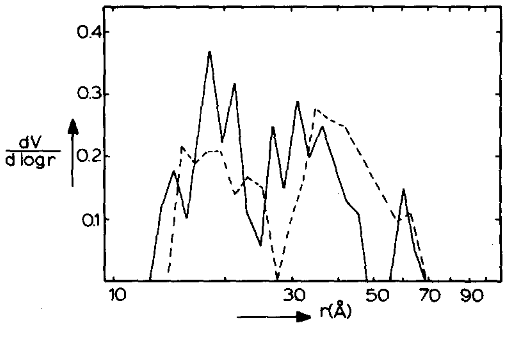

FIG. 3. Particle size distribution of catalyst U_{42}. (——) Prior to carburization–decarburization experiments, (– – –) after carburization–decarburization experiments.

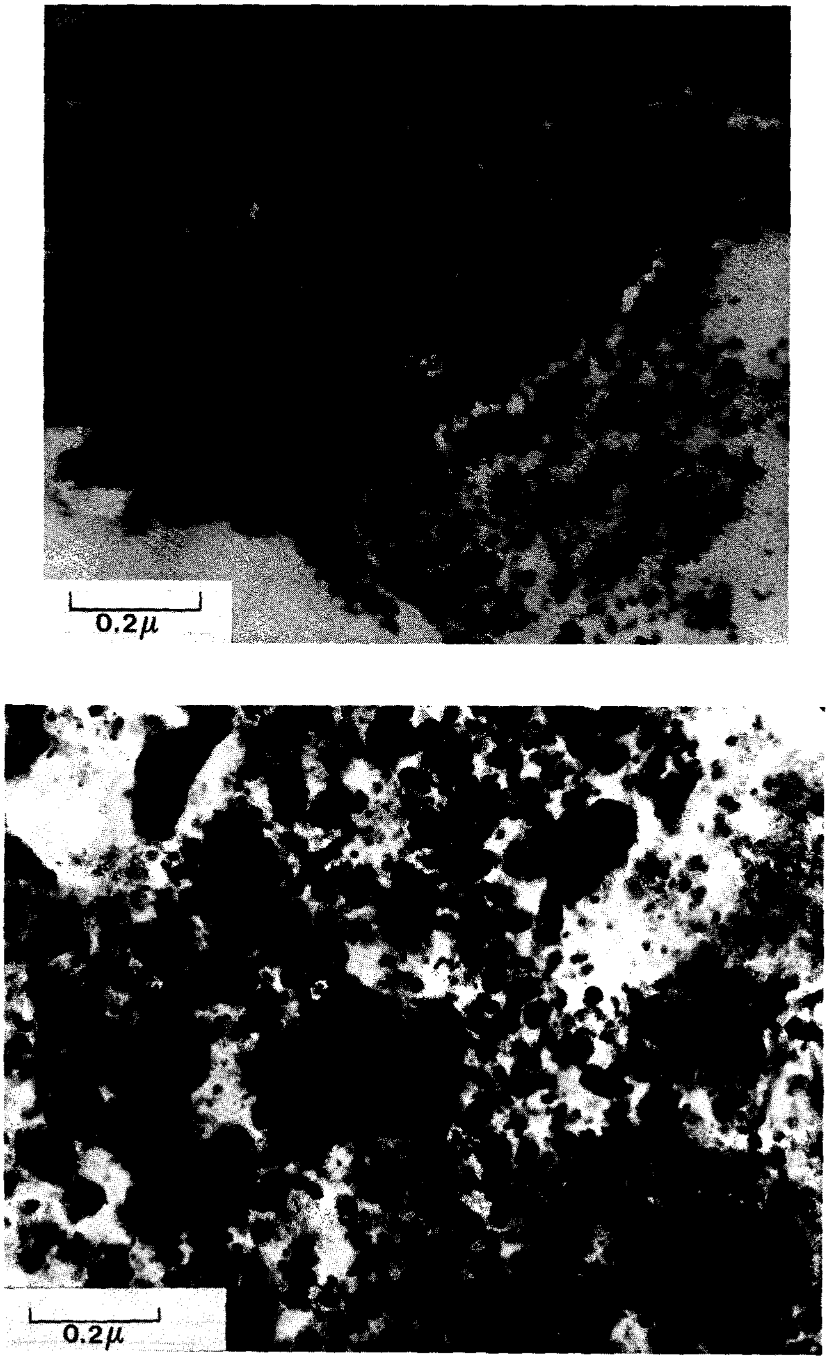

FIG. 4. Transmission electron micrographs of catalyst G_{65}. Above: after reduction at 450°C. Below: after reduction at 625°C.

sorption. Nickel atoms have been shown to be highly mobile over Ni surfaces (*5*). Nevertheless, even prolonged treatment of catalyst G_{65} in hydrogen at 625°C did not restore the original, lower activity for the decomposition of methane. We therefore have to accept that a very small number of strongly bound carbon atoms remains in the surface after treatment with H_2 at 450 or even 625°C, thus inhibiting the relaxation of the surface to its original state. Reportedly (*6*) carbon atoms strongly reduce the mobility of tungsten atoms on tungsten surfaces, and apparently on nickel they operate analogously. On the carbon-containing, reconstructed surface more hydrogen can be chemisorbed and the activity for the decomposition of methane is higher. A rearrangement of iron surfaces brought about by sorption of carbon atoms (and a corresponding increase in the sorption capacity of the catalyst) has also been found by Kieffer (*7*). This author also observed that the surface remained reconstructed during temperature-programmed reduction with H_2. Frennet and Liénard (*8*) have reported an increase in the surface area of their nickel films in a study of the decomposition of methane. The authors conclude that a reconstruction of the surface proceeds proportionally to the number of sorbed carbon atoms. A similar rearrangement of the surface nickel atoms may also explain the results reported by Araki and Ponec (*9*), who studied the methanation reaction on Ni films. Starting with a mixture of ^{12}CO and H_2 they observed that the initial rate of $^{12}CH_4$ formation on a film with preadsorbed ^{13}C was larger than on the bare film. Our results suggest that the preadsorbed ^{13}C brought about a change in the surface structure of the film leading to an enhanced methanation activity.

Recently Coenen *et al.* (*10*) and van Meerten *et al.* (*11*) have mentioned a rather peculiar behavior of Ni/SiO_2 catalysts during the methanation reaction. Although they observed by means of magnetic measurements that the mean diameter of their nickel particles increased substantially during the reaction at 208°C, the activity of their catalysts hardly changed. Stated otherwise, the activity per unit surface area of nickel increased, while the activity per gram of nickel did not change. According to the authors the growing particle size is to be ascribed to sintering by transport of nickel from small to large particles via nickel carbonyl, $Ni(CO)_4$. When the growth of the Ni particles with the consequent decrease in S_{Ni} and in catalytic activity balances the increase in activity brought about by the reconstruction of the surface during the methanation reaction, the overall activity can be expected to remain almost constant.

Coenen *et al.* (*10*) and van Meerten *et al.* (*11*) also measured the extent of H_2 chemisorption on their samples after 11 h of methanation. In agreement with their magnetic results a decrease in S_{Ni} was found. Our results, however, show that on the reconstructed surface more hydrogen can be chemisorbed per unit surface area of Ni (Figs. 1 and 2). The difference between their results and ours must be due to a different pretreatment of the catalyst prior to hydrogen chemisorption. The carbon was removed from our samples by heating to 450°C in H_2, whereas the carbon deposits of van Meerten *et al.* were removed by exposure to air at 450°C, followed by a re-reduction in H_2. As dealt with above, the treatment in H_2 alone does not eliminate all surface carbon. As long as the surface contains carbon atoms, the relaxation to its bare state is inhibited. When, however, carbon is burned off in air, no carbon is left in the surface, and the original surface structure is restored.

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