ELIMINATION OF THE WATER–GAS SHIFT REACTION BY DIRECT PROCESSING OF $CO/H_2/H_2O$ OVER Ni/SiO_2 CATALYSTS

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Summary

Methanation of CO-rich gases without a prior water–gas shift reaction requires nickel catalysts which are not susceptible to deactivation by the deposition of filamentous carbon. In an extensive study of the nucleation, growth and termination of the carbon filaments, the results of which are reported, it was found that even at low H_2/CO ratios the growth of carbon filaments can be avoided by the use of advanced catalysts in which substantially all nickel particles are bonded to the support by means of an interfacial oxidic layer. Such catalysts can, for instance, be prepared according to the method of deposition–precipitation from a homogeneous solution. With catalysts thus prepared very prolonged (up to 1000 h) experiments were carried out at pressures up to 600 kPa, in which H_2/CO mixtures of various compositions were converted to methane. To maintain a constant activity of the catalysts, addition of steam was necessary only when the H_2/CO ratio of the reaction mixture was below unity. At higher H_2/CO ratios, addition of steam was not required. It was established that even in the complete absence of hydrogen, carbon monoxide could be quantitatively converted into methane and carbon dioxide with steam as the only reactant and without any loss of catalytic activity over 1000 h.

Introduction

Gasification of coal with steam/oxygen produces coal gas which mainly contains carbon monoxide and hydrogen. The H_2/CO ratio of the coal gas depends on the particular gasification process, and generally is between 0.5

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and 2.0. After purification, coal gas can be utilized for the catalytic production of methane. In view of its elevated selectivity and relatively low price, nickel still is the pre-eminent catalyst for methanation. Before catalytic methanation, the H_2/CO ratio must be adjusted to three or more to meet the stoichiometry of the reaction: $CO + 3H_2 \rightarrow CH_4 + H_2O$. The catalytic water-gas shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$, is generally utilized to adjust the H_2/CO ratio. Catalysts frequently used for this reaction are Fe_2O_3/Cr_2O_3, $Cu/ZnO/Cr_2O_3$ and $CoO-MoO_3/Al_2O_3$ [1].

To produce substitute natural gas (SNG) at lower investments and a better thermal efficiency, combination of the water-gas shift reaction and methanation into one step would be very attractive [2, 3]. Such a combination requires a methanation catalyst which also catalyses the following reactions:

$$2CO + 2H_2 \longrightarrow CH_4 + CO_2$$

$$4CO + 2H_2O \longrightarrow CH_4 + 3CO_2$$
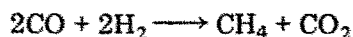
Conventional nickel catalysts are not likely to be suitable for the latter two reactions since they are susceptible to deactivation by carbon deposition.

Carbon deposition is a serious problem, even with a large excess of hydrogen. Agrawal *et al.* [4] reported that the methanation activity of a Ni/Al_2O_3 catalyst in a mixture of 4% CO and 96% H_2 decreased by 10% (at most) per 24 h ($T < 400$ °C). Knowing that deactivation of nickel catalysts proceeds even at high H_2/CO ratios, it can be expected that catalysts that are exposed to gas mixtures having a H_2/CO ratio lower than 2 will lose their activity at a much higher rate. Bartholomew *et al.* [5] observed that Ni/Al_2O_3 catalysts lost 20 - 60% of their original methanation activity after treatment in a gas mixture of $H_2/CO = 2$ at 675 - 700 K for 10 - 15 h. On the other hand, it is known that addition of water vapour to the reaction mixture reduces the deposition of carbon [6]. The favourable influence of water can be ascribed to the reaction between surface carbon atoms and H_2O according to $2C + 2H_2O \rightarrow CH_4 + CO_2$ [7, 8] or, at low carbon surface coverage, also to $C + 2H_2O \rightarrow CO_2 + 2H_2$ [8]. In industrial pilot plants for the direct production of SNG from coal gas, large amounts of steam are added to the coal gas, not only to provide the balance of the hydrogen required to complete the process of producing methane from carbon, but also to cause the overall composition of the gas mixture to be situated outside the area where carbon deposition should thermodynamically proceed [3]. The addition of large amounts of steam, however, has several drawbacks. First of all it is expensive and secondly, if the space velocity must remain constant, it calls for a reactor with a larger volume because of the resulting larger throughput of gas.

The aim of the present work was to develop a catalyst which has a high, stable activity for the direct methanation of CO-rich gases without the addition of large amounts of steam, near, or even within, the area where carbon should be formed thermodynamically. To that end we first studied in detail

the deposition of carbon on conventional nickel catalysts, using transmission electron microscopy both in bright and dark fields. Catalysts were fouled by carbon under reaction conditions at low H_2/CO ratios. Based on the results of this study, special nickel catalysts have been developed. The catalysts were used in direct methanation tests, with and without the addition of steam, and the results of these tests are presented.

Experimental

Two catalysts were used in the direct methanation tests. Catalyst A was a commercially available nickel catalyst, which was pretreated following the instructions of the manufacturer. According to the specifications the catalyst contained 55.76 wt.% of nickel on a Kieselguhr carrier. When reduced properly, 54% by weight of the total amount of nickel is in the metallic state. Catalyst B 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. [9] and Hermans and Geus [10]. 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 pellets of dimensions between 0.7 and 2.0 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 h at 450 °C. The degree of reduction was determined both thermogravimetrically and magnetically 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 1.33 kPa; from the amount of hydrogen absorbed at 33.3 kPa 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 used.

The methanation experiments were carried out in a completely automatized equipment, which was controlled by a Hewlett Packard 85 microcomputer. With all gases a constant mass-flow rate was obtained by means of pressure and (electronic) flow controllers. Before the reactant gas mixture reached the reactor, it was passed through a preheater. When addition of steam to the reaction mixture was required, an accurate flow of liquid water was introduced into the preheater. The reactor was a cylindrical stainless steel tube (diameter 1.8 cm, length 17 cm). The temperature of the catalyst bed was monitored at 9 equidistant heights along the axis of the catalyst bed. To establish whether catalyst plugging occurred, the pressure drop over the reactor was recorded continuously. By means of a back-pressure regulator, the total pressure in the reactor was kept constant at a level of 600 kPa.

Analysis of the gas phase was performed gas chromatographically. A Hewlett Packard 5840A gas chromatograph equipped with a Porapak Q column was used with N_2 as the carrier gas. After separation of the components and subsequent passage through a hot-wire detector (HWD), CO and CO_2 were converted catalytically into CH_4 by the H_2 feed of the flame-ionization detector (FID), which was put in series with the methanation catalyst. The HWD was used for the quantitative determination of H_2, whereas the FID was applied for the carbon-containing components.

Catalyst samples to be studied in the electron microscope were pulverized in a mortar and subsequently ultrasonically treated in ethanol (96%) for at least 5 min. A drop of the suspension thus obtained was put onto a filmed copper grid. To reinforce the specimen, a thin layer of carbon was vapor-deposited. Investigation of the samples was carried out in either a Philips EM 301, EM 420 or a JEOL 200C electron microscope.

Results and discussion

Carbon filament growth

A sample of catalyst A was calcined and reduced appropriately, and subsequently exposed to a reaction mixture containing 10% CO, 15% H_2 and 75% N_2 at a total pressure of 600 kPa and at a space velocity of 1200 h^{-1}. The temperature of the gas mixture at the inlet of the reactor was 250 °C. After an initial period of about 70 h, the pressure drop over the catalyst bed began to increase sharply, eventually leading to plugging of the reactor after about 230 h (Fig. 1).
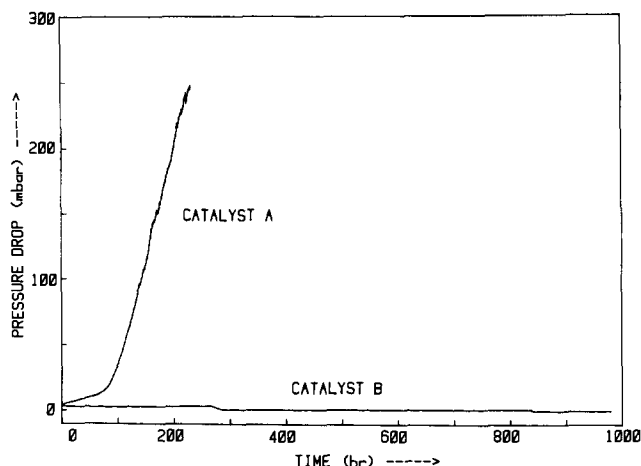

Fig. 1. Pressure drop over the reactor as a function of time. Input gas composition 10% CO, 15% H_2 and 75% N_2; space velocity 1200 h^{-1}; total pressure 600 kPa; reactor inlet temperature 250 °C. Catalyst A: conventional nickel catalyst; Catalyst B: catalyst prepared according to the method of deposition–precipitation from a homogeneous solution.
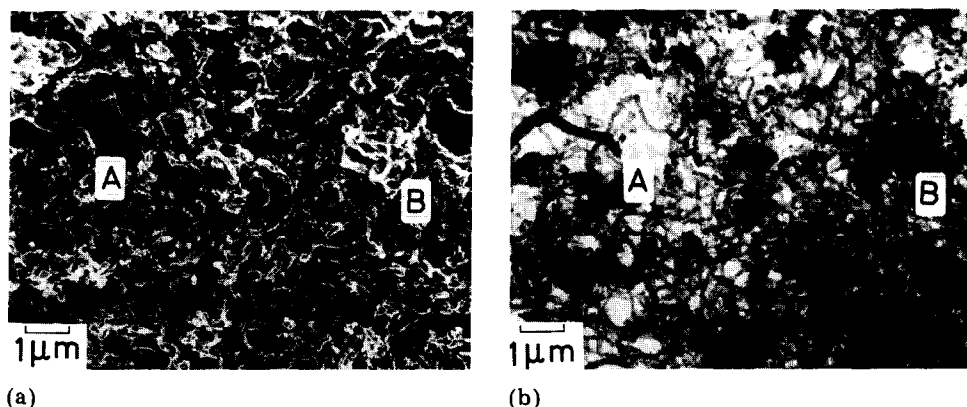
Fig. 2. Electron micrograph showing a network of carbon filaments deposited during methanation of a CO-rich gas. (a): scanning electron micrograph indicating the morphology of the sample; (b): the same area in a scanning transmission electron micrograph. In between the carbon filaments fragments of the original catalyst bodies can be observed. A and B indicate the same spots.

The catalyst at the entrance of the reactor, which originally was present as pellets of dimensions between 0.7 and 2.0 mm, turned out to be completely pulverized. Chemical analysis of the powdered material which plugged the reactor revealed that it contained up to about 10 wt.% of carbon. Electron microscopic analysis of the powder showed that the catalyst bodies originally present were broken up by the growth of large filaments. This is illustrated in Fig. 2. The generation of large filaments during the reaction, coupled with a strong increase in the carbon content of the catalyst, provides evidence that the filaments mainly consist of carbon. The formation of such filamentous carbon in supported nickel catalysts has been extensively studied by Baker and coworkers using controlled atmosphere electron microscopy [11, 12]. Whereas these authors were concerned mainly with the catalytic decomposition of· hydrocarbons, especially of acetylene, other workers have reported on the growth of carbon filaments in nickel catalysts during the disproportionation of carbon monoxide [6, 13] and during the methanation reaction [6].

To account for the growth of the filaments Baker *et al.* [11] proposed a mechanism which can be summarized as follows: carbon atoms, generated at the surface of the nickel particles by the dissociative chemisorption of a hydrocarbon or of carbon monoxide, dissolve in the nickel and migrate through the metal to the interface of the particle with the support. At the interface, nucleation of carbon atoms proceeds and subsequently a polymeric filament begins to grow. Since the filament grows out exclusively at the metal–support interface, the metal particle is forced away from the support. In this way a network of filaments, each with a nickel particle at its growing end, is created, as is seen in Fig. 2. The proposed mechanism rationalizes the fact that the width of the growing filament is always about equal

Fig. 3. Electron micrograph showing a faceted nickel particle at the head of a carbon filament. Note also that the filaments are locally less electron-transparent.

to the diameter of the nickel particle at its top. This is illustrated in Fig. 3, which shows an example of a faceted nickel particle on top of a filament of about the same diameter.

In Fig. 3 it can be seen that locally the filaments are less electron-transparent. The poor transparency can be brought about by inhomogeneities in the thickness of the sample, or, alternatively, by the presence of crystalline material of an atom number higher than carbon. To distinguish between these two possibilities, samples were studied electron microscopically in both bright and dark fields. In Fig. 4 two micrographs of the same sample in both bright and dark fields are shown. With the dark field micrograph, the incident beam has been tilted to such an extent that electrons coherently diffracted by the nickel particle at the top of the filament can pass through the objective lense aperture. Also in the same micrograph, the dark platelets observed in bright field in the interior of the filament show up brightly, which provides evidence that these platelets are small nickel crystallites. The nickel crystallites inside the filament cannot but originate from the nickel particle at the top of the filament. Apparently, the nickel particle catalysing the growth of the carbon filament gradually wears off during the process. Subsequently, the disappearing nickel nucleates inside the filament to new, small nickel crystallites. As these crystallites are almost completely encapsulated by carbon, they no longer contribute to catalytic activity.

The gradual disappearance of the nickel particles at the top of the filaments is also clear from the occurrence of filaments on top of which the nickel particle is completely absent. The tapering end of these filaments is particularly remarkable, as can be seen in Fig. 5. As we have already noticed, the width of the filament is always about the same as the diameter of the nickel particle catalysing its growth. Apparently, the nickel particle at the top of the growing filament initially only flattens, but just before completely vanishing rapidly assumes a smaller diameter. The tapering end of the filaments, as shown in Fig. 5, can then be accounted for by the eventual
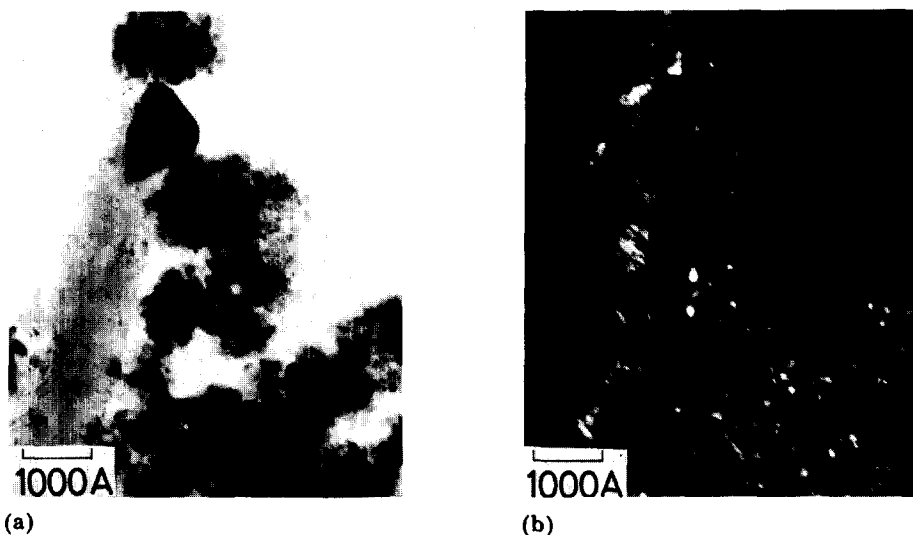
Fig. 4. Electron micrograph of a catalyst sample, both in bright (left) and dark (right) fields, showing the presence of small nickel crystallites in the interior of the carbon filament.
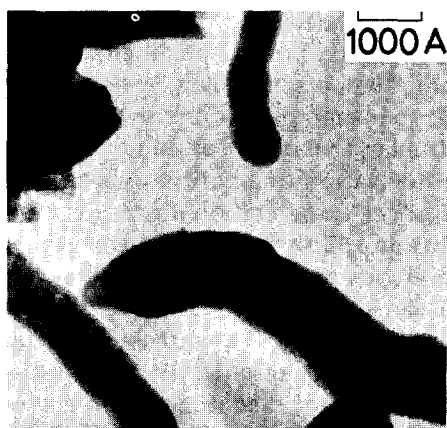

Fig. 5. Electron micrograph showing a carbon filament without a nickel particle at the top. Note the tapering head of the filament.

rapid decrease in diameter of the nickel particle. After the original nickel particle has disappeared completely, the filament growth is terminated.

Careful inspection of the filaments in Figs. 3 and 4 reveals that the nickel crystallites which have nucleated in the interior of the filaments are mainly situated at the outer filament edges, which consequently are less electron-transparent. Baker *et al.* [11, 12] also reported the filament wall to be more dense than the inner core material. To explain their observations, the authors assumed the filament wall to be constituted from carbon atoms

which, instead of dissolving into the bulk of the nickel particle, have migrated to the filament by surface diffusion. The carbon layer subsequently formed by these atoms would show more structural order owing to the larger contact time of the surface carbon with the nickel. However, this explanation cannot hold true in all circumstances. Under the experimental conditions we described above, the amount of surface carbon is strongly reduced as a result of the rapid reaction between adsorbed carbon and H_2 [8, 14]. Consequently, the build-up of a more ordered filament skin from surface carbon atoms does not proceed. In view of the above, the less transparent filament wall observed by Baker *et al.* may alternatively be explained by the presence of small nickel platelets mainly at the outer edges of the filaments.

According to the mechanism outlined above, the rate of filament growth is governed by the solubility of carbon in nickel metal on the one hand, and by the rate of diffusion of dissolved carbon atoms through the bulk of the nickel particles on the other hand. It is commonly accepted that the rate-determining step in the process is the diffusion of carbon through the nickel [15]. This is concluded from the close agreement between the experimentally observed activation energy for filament growth and the value determined for carbon diffusion in nickel. Moreover, the overall reaction is zero order. In earlier work [8, 16] we reported that the solubility of carbon deposited from CO onto small nickel particles by far exceeds the solubility of graphitic carbon in bulk nickel. Whereas the latter is known [17] to be smaller than 0.1 at.% at 275 °C, the uptake of carbon by small supported nickel particles surpasses 14 at.% at the same temperature. The carbon taken up is partly dissolved interstitially, while another part is involved in the formation of bulk nickel carbide. We feel the larger carbon solubility in small nickel particles to be due to the difficult nucleation of a continuous carbon layer at the surface. As nucleation cannot proceed, the carbon atoms dissolve into the nickel rather than remain in an amorphous state at the surface. Nucleation of the dissolved carbon, however, is apparently facilitated at the rear of the particle, at the interface with the support. This is in agreement with the observations of Rostrup-Nielsen and Trimm [18], who ascribed the easier nucleation at the rear of the particle to the presence of (screw) dislocations. After nucleation at the metal–support interface, the carbon grows out between the particle and the carrier, as set out in detail above. We have argued that the characteristic feature of this growth process is the disruption of the nickel particle from the support. When one succeeds, by any means, to adhere the nickel particle strongly to the carrier, initiation of the filament growth can be expected to be severely hampered. This idea led to the development and use of catalysts whose the nickel particles are chemically bonded to the carrier. In the next paragraph the results obtained with these catalysts are described.

Simultaneous water–gas shift and methanation

As pointed out in the Introduction, direct methanation of the purified CO-rich gas produced in a coal gasifier would be very attractive. To achieve

this a catalyst should be used which, for reasons already discussed in the previous section, is characterized by a strong bonding between the nickel particles and the support. The most obvious way to effect a strong chemical bond between the metal and the oxidic carrier is partial reduction of the nickel hydroxide or nickel oxide primarily fixed on the carrier. It is known from the literature [19] that oxidation of a metal at the interface with an ionic substrate causes the metal to be chemically bonded to the substrate, whereas the adhesion of clean metal surfaces to ionic carriers is due to Van der Waals forces only. There is a problem, however, in that the reduction of a nickel oxide particle, once started, tends to proceed rapidly until the particle is fully reduced to nickel metal. Therefore, at least part of the nickel ions should be supplied in a form which can be reduced more slowly than the pure oxide. This can, for instance, be accomplished by preparing a catalyst as described for catalyst B in the experimental section. As has been shown by Hermans and Geus [10], catalysts thus prepared contain an appreciable fraction of the nickel in the form of a nickel hydrosilicate, $Ni_3(OH)_3$-Si_2O_5OH (antigorite), which is difficult to reduce completely. The elevated reduction temperature of this compound is illustrated in Fig. 6, which shows the temperature-programmed reduction of a sample of catalyst B, previously reduced at 450 °C and reoxidized at 440 °C. In the DTG-signal two minima are observed. The first minimum represents the reduction of the NiO phase, which was generated during the reoxidation after the first reduction. The second minimum in the graph, at a temperature above 600 °C, relates to the reduction of the nickel hydrosilicate phase, which obviously was resistent to the first reduction at 450 °C. It can also be deduced from Fig. 6 that under the reaction conditions not all of the nickel is in the reduced state. The partially reduced nickel particles are chemically bonded to the silica support by an interfacial layer consisting of nickel hydrosilicate. The presence of the chemical bond inhibits the nucleation and subsequent growth of carbon filaments at the interface between the nickel metal and the silica.
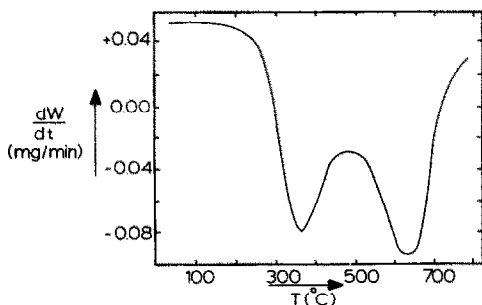

Fig. 6. Differential Thermal Gravimetric (DTG) plot for the reduction of a sample of catalyst B, previously reduced at 450 °C and reoxidized at 440 °C. Reduction was established in a flow of 10% H_2 in Ar; heating rate 5 °C min^{-1}. Catalyst B was prepared according to the method of deposition–precipitation from a homogeneous solution.

TABLE 1

Experimental conditions and results of some direct methanation tests (space velocity: $1200 \ h^{-1}$)

Experiment	Reactor temperature ($C°$)		Reactants (vol%[a] on a dry basis)			Water addition (mmol min^{-1})	Products (vol% on a dry basis)					Dura-tion (h)
	inlet	outlet	H_2	CO	N_2		CH_4	CO_2	H_2	CO	N_2	
a	250	230	15.0	10.0	75.0	—	6.9	4.1	—	0.2	88.8	1000
b	260	190	26.9	17.9	55.2	—	14.0	8.2	—	0.2	77.6	650
c	350	370	11.8	23.5	64.7	49	8.1	15.6	6.8	1.1	68.4	500
d	350	386	—	11.2	88.8	29	2.3	8.3	1.1	0.1	88.4	1100

[a]$1 \ vol\% = 0.056 \ Nl \ min^{-1}$.

Figure 1 shows the results which were obtained when a sample of catalyst B was subjected to the same experiment as described above for catalyst A. A gas mixture comprising 10% CO, 15% H_2 and 75% N_2 was passed through the catalyst bed at a space velocity of $1200 \ h^{-1}$ and a total pressure of 600 kPa. The temperature of the reaction mixture at the entrance of the bed was 250 °C. The product gas, the composition of which did not change during the experiment, consisted of 6.9% CH_4, 4.1% CO_2, 0.2% CO and N_2; the H_2O content was not determined quantitatively. After 1000 h the activity of the catalyst had not decreased and no increase in pressure drop was observed. The pressure drop being at a constantly low level indicates the absence of carbon filament growth and consequent reactor plugging. The impediment of carbon filament growth was confirmed by electron microscopic analysis.

Many more prolonged experiments were performed using the same catalyst B. In these experiments H_2/CO mixtures of various compositions were converted to methane at a total pressure of 600 kPa. The results of some of these experiments are summarized in Table 1. From the data in Table 1 and from the observed constancy of the temperature profiles in the reactor, it can be concluded that catalyst B displays a stable activity in catalysing the following three reactions:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

$$2CO + 2H_2 \longrightarrow CH_4 + CO_2$$

$$4CO + 2H_2O \longrightarrow CH_4 + 3CO_2$$
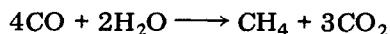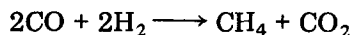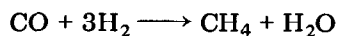
Only when the H_2/CO ratio of the mixture is below unity is the addition of steam necessary to attain complete CO conversion and to maintain a constant activity. From experiment d it is clear that even in the complete absence of hydrogen, CO can be quantitatively converted with H_2O to CH_4 and CO_2. Experiment d illustrates that nickel is far from being a suitable catalyst for the CO shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$. Instead of CO_2 and H_2, a

mixture of CH_4 and CO_2 is produced from CO and H_2O. As we have explained before [16], this is due to the dissociative nature of CO adsorption on nickel. The carbon atoms chemisorbed react with water according to: $2C + 2H_2O \rightarrow CH_4 + CO_2$.

In conclusion we would like to state that nickel catalysts characterized by a chemical bonding between the metal particles and the support are very suitable for the conversion of CO-rich gases simultaneously with H_2 and H_2O. It must be emphasized, however, that the processing of high CO partial pressures at too low a temperature gives rise to the generation of gaseous $Ni(CO)_4$ and, consequently, to sintering of the nickel crystallites [20]. Nickel particles deposited upon the support from $Ni(CO)_4$ no longer are chemically bonded, and therefore are susceptible to carbon filament growth. Moreover, when the particles grow too large, they may contain grain boundaries, which also can act as nucleation centers for carbon filaments [21].

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