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Metal–Support Interaction: Titania-Supported and Silica-Supported Nickel Catalysts

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The influence of the nature of the support on nickel catalysts behaving as methanation or Fischer–Tropsch catalysts is studied. This has been done by varying the support (silica and titania), the nickel loading (2–20 wt.%) and the reduction temperature (573–773 K). For *in situ* characterization of the supported nickel catalysts magnetic measurements have been performed. Silica-supported nickel catalysts show a very high selectivity toward methane, which does not depend on the nickel loading or the reduction temperature. Highly loaded (20 wt.%) titania-supported nickel catalysts which are reduced at relatively low temperatures, also show this methanation behavior. However, high-loaded catalysts reduced at high temperatures as well as low-loaded catalysts show the production of high amounts of higher hydrocarbons. The nature of the carbon present at the surface of the catalyst during Fischer–Tropsch synthesis is different for the catalysts which produce methane and for the catalysts which show the production of higher hydrocarbons. These differences between the two groups of catalysts are most probably due to an interaction between nickel and TiO_x ($x < 2$) species, which can cover part of the nickel particles. The TiO_x species promote the dissociation of CO and decrease the hydrogen dissociation rate. This change in dissociation properties can probably cause the change in the product selectivity and the different types of carbon present at the surface.

INTRODUCTION

Metal–support interactions as known to have a large influence on the catalytic properties of supported catalysts, especially when reducible materials such as titania or thoria are used as supports (1, 2). Fischer and Meyer showed in 1931 the large effect of thoria on the production of hydrocarbons using nickel on kieselguhr catalysts (1). Tauster (2) described a remarkable decrease of the H_2 and CO chemisorption properties of titania-supported metal catalysts due to a strong metal–support interaction (SMSI). The nature of this interaction was explained by the presence of partly reduced TiO_x species at the surface of the metal. Vannice and Garten (3) found that titania-supported nickel catalysts were more active and selective toward the formation of higher hydrocarbons from CO/H_2 mixtures than alumina-supported nickel catalysts. Furthermore, varying the nickel loading did not change the performance of the catalyst. De Bokx (4) showed that the calcination temperature appreciably affects the reduction behavior of titania-supported nickel catalysts. After a high-temperature calcination (723 K) a nickel titanate phase had been formed. The behavior during calcination and reduction turned out be independent of the metal loading. Bartholomew *et al.* (5) also reported that titania- and alumina-supported nickel catalysts give more higher hydrocarbons in Fischer–Tropsch synthesis than silica-supported nickel catalysts. In contradiction to De Bokx (4) and Vannice and Garten (3) these authors found an influence of the nickel loading on the performance of the catalyst. Turlier *et al.* (6), who studied the behavior of nickel on different supports, found an increase of the C_{2+} selectivity with unsupported and with titania-supported nickel catalysts in comparison to silica-supported nickel catalysts. This was explained by a dilution effect caused by the presence of Ni^{2+} ions near active sites at the surface of the catalyst (6).

In this study the influence of the support on nickel catalysts in the Fischer–Tropsch synthesis by varying the support (titania and silica), the nickel loading (2–20 wt.%), and the reduction temperature (573–773 K) is investigated. Since nickel produces mainly methane upon exposure to a carbon monoxide-hydrogen flow, any effect of the support on the selectivity of the supported nickel particles will be readily apparent.

METHODS

Catalyst Preparation

Precursors of the titania- and silica-supported nickel catalysts were prepared by controlled injection (1 ml/min) of a nickel nitrate solution (0.22 M) into a suspension of the support in 1.5 liter demineralized water. As supports were

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TABLE 1

The Particle Size of the Calcined Catalysts as Determined from XPS

Catalyst	Particle size (XPS) (Å)
$2Ni/TiO_2$	12
$5Ni/TiO_2$	18
$10Ni/TiO_2$	19
$20Ni/TiO_2$	49
$2Ni/SiO_2$	25
$10Ni/SiO_2$	57
$20Ni/SiO_2$	106

used Degussa OX50 (silica, 50 m^2/g) and Degussa P25 (titania, 50 m^2/g). The pH was maintained at a level of 9 by simultaneous injection of a solution of ammonia (1.5 *M*). After precipitation the precursors were washed with 1 liter demineralized water, dried in vacuum for 20 h at room temperature, pressed to tablets, and crushed. From the crushed material sieve fractions of 150 to 425 μm were collected. The catalyst precursors were calcined in air at 573 K for 3 h. The catalyst code used is *x*Ni/support, in which *x* is the calculated metallic nickel loading. By *in situ* reduction titania-supported catalysts were prepared with a total metal loading of 2, 5, 10, and 20 wt.% nickel and silica-supported catalysts with a nickel loading of 2, 10, and 20 wt.% (Table 1).

Fischer–Tropsch Synthesis

Fischer–Tropsch synthesis was executed in a fully automated microflow apparatus with a quartz reactor, i.d. 10 mm, operated at atmospheric pressure. The reaction products were analyzed by means of a Perkin–Elmer 8700 gas chromatograph equipped with a FID containing a methanizer. A Poropack Q column was used, which was operated between 353 and 473 K. Carbon monoxide, carbon dioxide and hydrocarbons from methane up to heptane were measured. About 350 mg of catalyst was reduced *in situ* in a 10% hydrogen in helium gas flow with a flow rate of 100 ml/min. During the reduction the temperature was linearly raised from 313 to 673 K at a rate of 1 K/min and subsequently kept constant for 9 h at 673 K. Then the reactor was cooled to 523 K and a synthesis gas mixture, with $H_2/CO = 2$ and a flow rate of 30 ml/min, was passed through the reactor for 6 h. The syngas concentration in helium was slowly increased to 100% in 30 min to prevent a large temperature increase in the catalyst bed due to the exothermic reaction.

Magnetic Measurements

Magnetic measurements were made to study the nature of the nickel phase under Fischer–Tropsch conditions. Fischer–Tropsch synthesis was performed after reduction of the catalyst precursor in a 50 ml/min 10% H_2 in helium gas flow at a heating rate of 1 K/min to 675 K and maintaining the temperature for 10 h. The synthesis reaction was executed using a 30 ml/min synthesis gas flow with a H_2/CO ratio of 2 at 525 K for 4 h. After Fischer–Tropsch synthesis the magnetization was also measured during temperature-programmed hydrogenation in 2% H_2/helium to assess the amount and nature of the carbon deposited during the synthesis.

The experiments were executed using a modification of a Weiss-extraction technique as described by Selwood (7). The apparatus, which has been described elsewhere (8), enabled us to perform *in situ* magnetization measurements in the temperature range of 295 to 850 K. Samples were measured at a constant magnetic field of 0.6 MAm^{-1} ($1\ MAm^{-1} = 1.26 \times 10^4$ Oersted).

Temperature-Programmed Hydrogenation

Temperature-programmed hydrogenation (TPH) experiments were executed to determine the nature and the amount of the carbon species present in catalysts after Fischer–Tropsch synthesis. The catalyst was cooled from the reaction temperature (525 K) to room temperature in a helium gas flow. Next, a 10% hydrogen in helium gas flow was passed through the catalyst bed and the temperature was increased from 300 to 873 K at a rate of 5 K/min. Carbon-containing compounds in the gas flow beyond the reactor were measured each minute with a Perkin–Elmer 8700 gas chromatograph.

Temperature-Programmed Reduction

To study the reduction behavior of the calcined catalysts Temperature-programmed reduction (TPR) experiments were performed. Calcined samples of 50 mg were placed in a quartz reactor whose temperature was linearly raised from 300 to 1123 K at a rate of 5 K/min, while a flow of 50 ml/min of 10% hydrogen in argon was passed through the sample. Water formed during the reduction was removed from the gas flow using a carbon dioxide/acetone cold trap. The hydrogen concentration was measured with a hot wire detector beyond the trap. The degrees of reduction were calculated by using a CuO reference compound, assuming 100% reduction of CuO to Cu.

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopic (XPS) measurements were executed with a standard Vacuum Generators MT 500/clam-2 spectrometer using Mg$K\alpha$ radiation produced by a Mg/Al anode. To calculate the particle sizes from the XPS data, a dispersion analysis program was used, which was based on a publication of Kuipers (9) as modified by Gijzeman (10).

RESULTS AND DISCUSSION

Particle Size Determination

To determine the particle size of the supported nickel oxide particles XPS measurements were executed. The results are presented in Table 1. It is found that the size of the nickel oxide particles increases with the nickel loading for both the titania- and the silica-supported catalysts. The particle size at equal loading turned out to be larger with silica-supported than with titania-supported catalysts, whereas the specific surface area is equal for both supports (50 m^2/g). During precipitation of the nickel ions onto the support the interaction between nickel ions and the carrier is presumably different with silica and titania, which can cause differences in nucleation and growth of the nickel compound species on silica and titania. However, it cannot be excluded that the difference in particle size may also be attributed to a different behavior of the silica- and titania-supported catalyst during calcination.

Temperature-Programmed Reduction

TPR measurements were executed to determine the reduction behavior of the various catalysts and to reveal whether the reducibility depends on the loading.

The reduction profiles of the calcined Ni/TiO_2 catalysts are presented in Fig. 1. The profiles of $2Ni/TiO_2$ and $5Ni/TiO_2$ show a broad hydrogen consumption pattern between 530 and 750 K, which most probably involves two different reduction steps, namely the reduction of NiO at low temperatures and subsequently the reduction of nickel titanate above 600 K. At higher nickel loadings the TPR profiles exhibit an increase of the low-temperature reduction step of NiO as well as an additional reduction step with an onset temperature of 373 K, which can be ascribed to the reduction of Ni_2O_3. The degree of reduction of all Ni/TiO_2 catalysts has been calculated to be 110 ± 10%. This degree of reduction higher than 100% will most probably be due to the reduction of Ti^{4+} to Ti^{3+} in the surface layers of the titania support by spillover of dissociated hydrogen from the nickel phase. Such a reduction of part of the TiO_2 support was also observed by Overbeek (11).

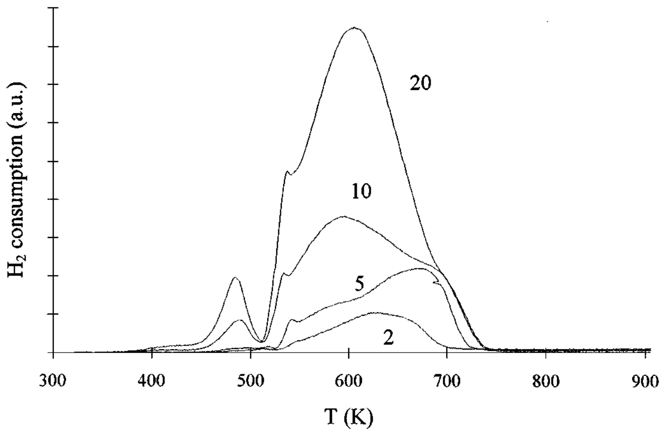

FIG. 1. TPR profiles of the titania-supported nickel catalysts: $2Ni/TiO_2$, $5Ni/TiO_2$, $10Ni/TiO_2$, and $20Ni/TiO_2$.

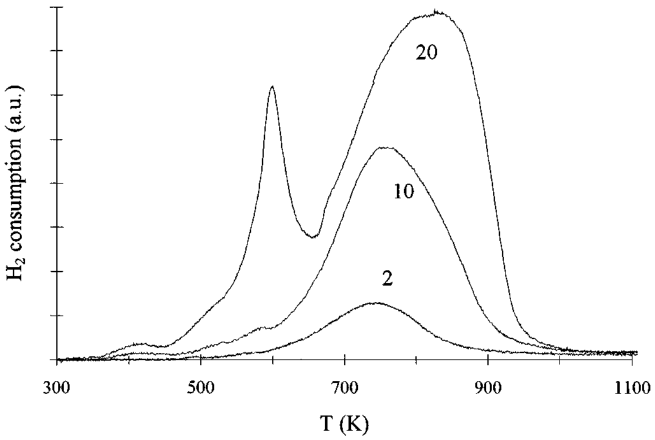

FIG. 2. TPR profiles of the silica-supported nickel catalysts: $2Ni/SiO_2$, $10Ni/SiO_2$, and $20Ni/SiO_2$.

The reduction behavior of the calcined Ni/SO_2 catalysts is shown in Fig. 2 and turned out to be clearly different from that of the titania-supported nickel catalysts. The reduction sets in at 373 K and is finished only at 973 K, which is at a much higher temperature than observed with the titania-supported catalysts. The TPR profiles of $2Ni/SiO_2$ and $10Ni/SiO_2$ show only one broad reduction peak with a maximum at 743 and 773 K, respectively, while the TPR pattern of $20Ni/SiO_2$ consists of two reduction steps, one with a peak maximum at 593 K and one at 843 K. The reduction at high temperatures is probably due to the reduction of nickel hydrosilicate, which was also found for a 30 wt.% Ni/SiO_2 catalyst as described by Brahma (12). The reduction step which takes place at low temperatures is most probably due to the reduction of NiO to metallic Ni as was also observed with the titania-supported catalysts. This NiO phase is probably present on top of the nickel hydrosilicate layer, whose nickel is much more difficult to reduce. The final degree of reduction of the silica-supported catalysts is calculated to be 100 ± 10%.

Fischer–Tropsch Synthesis

The CO conversion at 525 K as a function of the time on stream for the silica-supported catalysts is plotted in Fig. 3. The conversions, which do not significantly vary with time on stream, increase with the nickel loading. A higher nickel loading exhibits a higher activity of the reduced catalysts, due to the fact that a larger active surface area is available for Fischer–Tropsch synthesis. The selectivities toward CO_2, CH_4, C_2, and higher hydrocarbons (C_{3+}) are shown in Table 2. The selectivity toward CH_4 is more than 85% and also does not vary with time on stream. The Ni/SiO_2

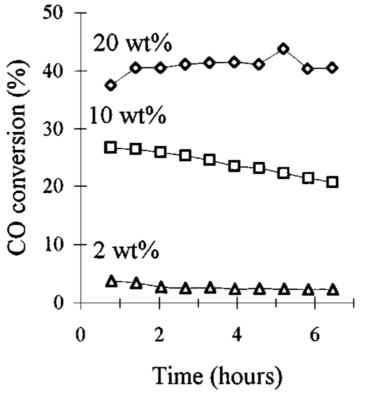

FIG. 3. CO conversion during Fischer–Tropsch synthesis for the 2, 10, and 20 wt.% nickel on silica catalysts after reduction at 673 K.

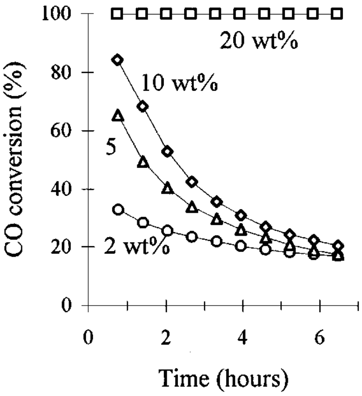

FIG. 4. CO conversion during Fischer–Tropsch synthesis for the 2, 5, 10, and 20 wt.% nickel on titania catalysts after reduction at 673 K.

catalysts behave like unsupported nickel catalysts. No influence of the SiO_2 support on the activity and selectivity has been observed (13).

The CO conversion as a function of time of the various titania-supported catalysts is presented in Fig. 4. The conversion of $20Ni/TiO_2$ is 100% and remains constant with time. The initial conversions of $2Ni/TiO_2$, $5Ni/TiO_2$, and $10Ni/TiO_2$ rise with increasing nickel loading from 33% to 84%. However, the CO conversion is not constant with time on stream for these catalysts and decreases from in initial values to about a level of 19% for the three Ni/TiO_2 catalysts after 6 h on stream. The selectivities toward CO_2, CH_4, C_2, and C_{3+} are also collected in Table 3. The selectivity toward higher hydrocarbons (C_{3+}) is shown in Fig. 5 and increases from 0% for $20Ni/TiO_2$ to 42% for $2Ni/TiO_2$ after 6 h of Fischer–Tropsch synthesis. The methane selectivity decreases from 80% for $20Ni/TiO_2$ to 37% for $2Ni/TiO_2$.

The $20Ni/TiO_2$ catalyst shows the behavior of a normal methanation catalyst, that is, a high and constant CO conversion with a high selectivity toward methane and no selectivity toward higher hydrocarbons. The production of 20% CO_2 and only 80% CH_4 is due to the fact that the synthesis gas feed has a H_2/CO ratio of 2. For 100% CH_4 selectivity at 100% CO conversion a H_2/CO ratio of 3 is required.

The increase of the C_{3+} selectivity with decreasing nickel loading up to 42% for $2Ni/TiO_2$ is rather remarkable. This cannot be ascribed to a change of the particle size only, because the silica-supported catalysts do not show such a particle size dependence. Therefore, the increase of the production of higher hydrocarbons has to be due to an influence of the titania support on the nickel active phase. Details about this influence will be discussed later.

The deactivation with time on stream of the $2Ni/TiO_2$, $5Ni/TiO_2$, and $10Ni/TiO_2$ catalysts is another important effect. This deactivation is probably caused by deposition of carbon, which apparently proceeds to a larger extent on larger particles, as the catalysts $5Ni/TiO_2$ and $10Ni/TiO_2$ display a more rapid drop in conversion. On unaffected nickel surfaces hydrogenation dominates over carbon monoxide dissociation, as is apparent from the fact that the conversion of the $20Ni/TiO_2$ catalyst does not drop with time on stream.

To determine the contribution of sintering to the deactivation of the catalysts, regeneration experiments were carried out. After 6 h of Fischer–Tropsch synthesis the catalyst

TABLE 2

Selectivities toward CO_2, CH_4, C_2, and C_{3+} after 6 h of Fischer–Tropsch Synthesis on Catalysts Reduced at 673 K

Catalyst	CO_2 (%)	CH_4 (%)	C_2 (%)	C_{3+} (%)
$2Ni/TiO_2$	5	37	16	42
$5Ni/TiO_2$	6	53	13	28
$10Ni/TiO_2$	6	59	12	23
$20Ni/TiO_2$	20	80	0	0
$2Ni/SiO_2$	0	87	4	9
$10Ni/SiO_2$	2	90	5	3
$20Ni/SiO_2$	2	90	5	3

TABLE 3

Selectivities toward CO_2, CH_4, C_2, and C_{3+} after 6 h of Fischer–Tropsch Synthesis on Catalysts Reduced at 573, 673, and 773 K

Catalyst	Reduction temperature (K)	CO_2 (%)	CH_4 (%)	C_2 (%)	C_{3+} (%)
$20Ni/SiO_2$	573	7	85	5	3
	673	2	90	5	3
	773	3	90	5	2
$20Ni/TiO_2$	573	21	78	1	0
	673	20	80	0	0
	773	3	54	13	30
$2Ni/TiO_2$	573	4	35	14	47
	673	5	37	16	42
	773	5	34	14	47

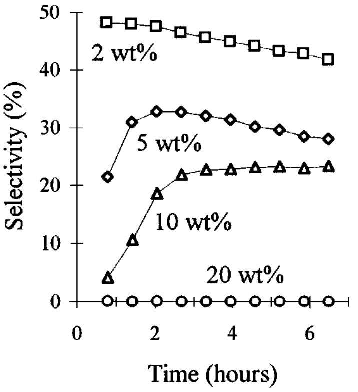

FIG. 5. Selectivity toward higher hydrocarbons (C_{3+}) for titania-supported nickel catalysts after reduction at 673 K.

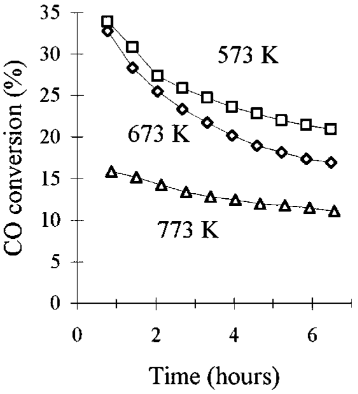

FIG. 7. CO conversion on $2Ni/TiO_2$ after reduction at 573, 673, and 773 K.

was hydrogenated in pure hydrogen to remove all carbon present in the catalyst. After this hydrogenation the activity of the catalyst was 99% of the original value, which indicates that the deactivation of the catalyst is mainly due to carbon deposition. The small decrease (1%) of the activity can probably be explained by sintering of the nickel particles during Fischer–Tropsch synthesis or during the hydrogenation.

To elucidate the effect of the support on the active nickel phase, the influence of the reduction temperature on the activity and selectivity was studied. In Fig. 6 the CO conversion as a function of time is shown for $20Ni/SiO_2$ reduced at 573, 673, and 773 K. The activity of this catalyst increases with increasing reduction temperature, due to an increasing amount of metallic nickel, as followed from the TPR pattern (Fig. 2). The selectivities measured after the different reduction procedures (see Table 3) are not affected by the reduction temperature. Therefore, the only effect of the reduction temperature on the $20Ni/SiO_2$ catalyst is the change in the degree of reduction and, consequently, the amount of active metallic nickel and thus the metallic nickel surface area present within the catalyst.

The CO conversion as a function of time for $2Ni/TiO_2$ after reduction at 573, 673, and 773 K is presented in Fig. 7. The initial conversion decreases with increasing reduction temperature, while irrespective of the reduction temperature the catalyst deactivates with time on stream. The decrease of the initial CO conversion may be attributed to the fact that at a higher temperature reaction of Ni(II) with titania to inactive nickel titanate proceeds at a more increased rate than the reduction of nickel oxide to metallic nickel. An alternative explanation may be a partial reduction of the titania surrounding the supported nickel particles and subsequently the reduced titania species, TiO_x ($x < 2$), migrates over the metallic nickel surface (14, 15). Additionally, it is found that the C_{3+} selectivity does not change significantly with the reduction temperature (Table 3).

In Fig. 8 the CO conversion is shown for $20Ni/TiO_2$ reduced at 573, 673, and 773 K. After reduction at 573 and 673 K the conversion is 100% and stays at this level, whereas after reduction at 773 K the initial CO conversion is only 72%, which additionally decreases with time on stream to 27% after 6 h of Fischer–Tropsch synthesis. Obviously, increasing the reduction temperature strongly decreases the

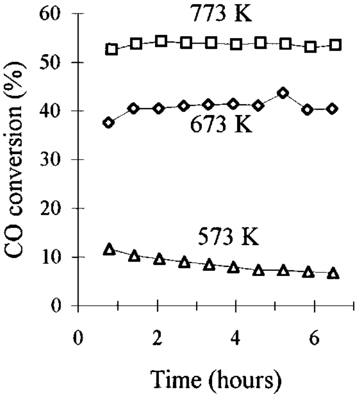

FIG. 6. CO conversion on $20Ni/SiO_2$ after reduction at 573, 673, and 773 K.

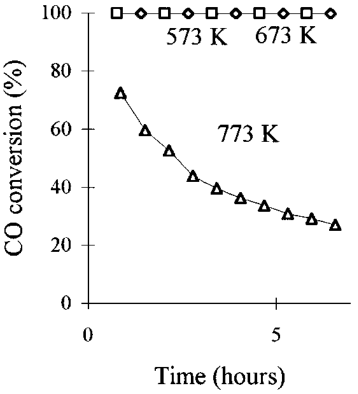

FIG. 8. CO conversion on $20Ni/TiO_2$ after reduction at 573, 673, and 773 K.

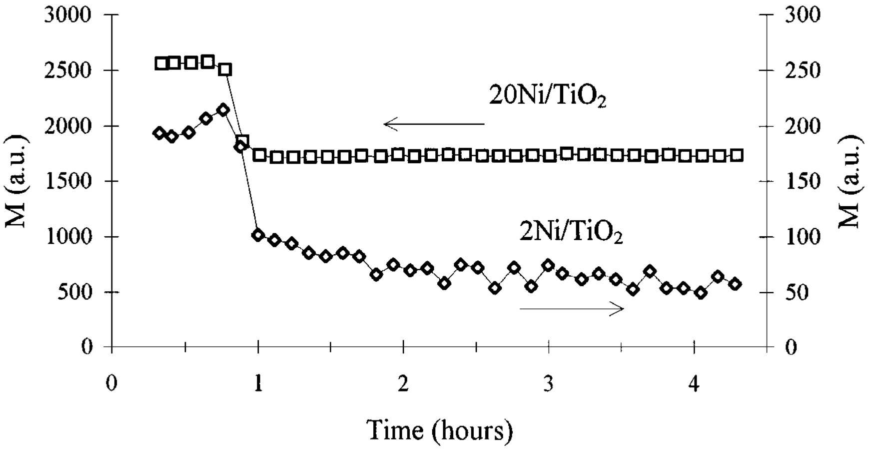

FIG. 9. Magnetization of $2Ni/TiO_2$ and $20Ni/TiO_2$ after reduction at 673 K during Fischer–Tropsch synthesis at 525 K.

CO conversion of $20Ni/TiO_2$, which is in contrast to the silica-supported catalyst. The C_{3+} selectivity is zero after reduction at 573 and 673 K; however, after reduction at 773 K the C_{3+} selectivity has become 30% (Table 3). Obviously, after reduction at 573 and 673 K a methanation catalyst is present, whereas after reduction at 773 K an active phase is present, at which a much larger production of higher hydrocarbons proceeds. After reduction at 773 K the $20Ni/TiO_2$ catalyst behaves in Fischer–Tropsch synthesis rather similarly to the $2Ni/TiO_2$ catalyst after reduction at lower temperatures.

Carbon Deposition during Fischer–Tropsch Synthesis

Magnetic measurements. Measurements were performed to study the nature of the supported nickel phase during Fischer–Tropsch synthesis. After reduction at 673 K the magnetization was measured as a function of time during Fischer–Tropsch synthesis at 525 K (Fig. 9).

The magnetizations of the $20Ni/TiO_2$ and $2Ni/TiO_2$ catalysts decrease very fast initially, from 2550 to 1750 a.u. and from 200 to 60 a.u., respectively, to remain subsequently constant during the next 4 h of Fischer–Tropsch synthesis. The relative decrease of the magnetization is 31% for $20Ni/TiO_2$ and no less than 70% for $2Ni/TiO_2$. The decrease of the magnetization must be caused by the formation of nickel carbides. As the magnetization does not decrease to zero during Fischer–Tropsch synthesis, either only surface carbides are formed and no bulk carbides or only a fraction of the nickel particles has reacted completely to nickel carbide. The difference in decrease of the magnetization between $20Ni/TiO_2$ and $2Ni/TiO_2$ can be explained by a different mean particle size, which causes a different surface/bulk ratio for the two catalysts or a larger fraction of the nickel particles completely reacted to carbides. When the decrease of the magnetization is due to the formation of surface carbides, the dispersion determines the relative decrease of the magnetization.

After Fischer–Tropsch synthesis a thermomagnetic analysis in 2% H_2/helium was executed (Fig. 10). The magnetization of $20Ni/TiO_2$ starts at 3500 a.u. and has become

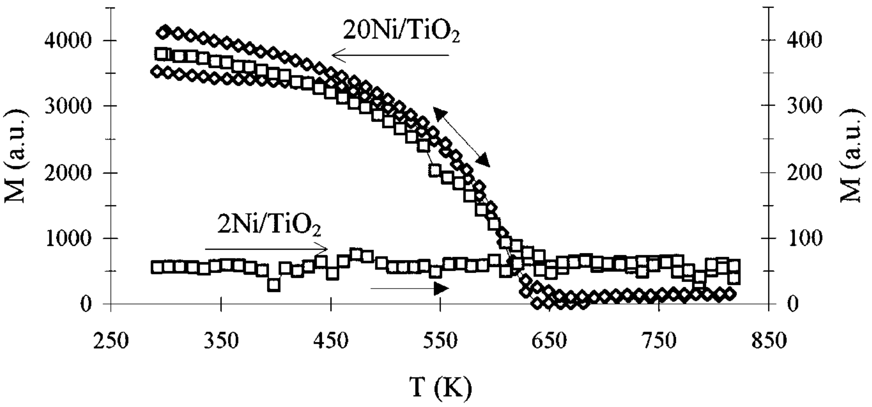

FIG. 10. Magnetization of $2Ni/TiO_2$ and $20Ni/TiO_2$ during temperature-programmed hydrogenation in 2% H_2 in helium after Fischer–Tropsch synthesis.

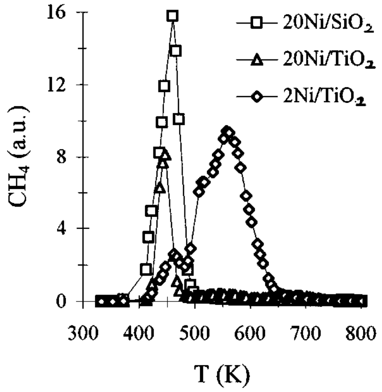

FIG. 11. Temperature-programmed hydrogenation experiments of 20Ni/SiO_2, 20Ni/TiO_2, and 2Ni/TiO_2 after reduction at 673 K and Fischer–Tropsch synthesis at 525 K.

4100 a.u. after the temperature-programmed hydrogenation cycle. The hydrogenation has already finished at about 500 K and the magnetization becomes zero at about 630 K, near the Curie temperature of nickel (628 K). The magnetization of 2Ni/TiO_2 is initially very low (50 a.u.) and remains low during the temperature increase. With decreasing temperature the magnetization rises and shows a normal nickel magnetization curve with a Curie temperature of about 630 K and a magnetization of 380 a.u. at room temperature.

Temperature-programmed hydrogenation. TPH experiments were performed to determine the nature and the amount of carbon present on the catalysts after 6 h of Fischer–Tropsch synthesis. After the hydrogenation step a temperature-programmed oxidation in air was performed. However, no carbon-containing products were observed during this oxidation. Obviously, all carbon present in the catalysts was removed during the hydrogenation step. In Fig. 11 the TPH patterns are shown of the 20Ni/SiO_2, the 20Ni/TiO_2, and the 2Ni/TiO_2 catalysts, previously reduced at 673 K. In Table 4 the amounts of carbon calculated from the TPH patterns are collected. The TPH profile of 20Ni/SiO_2 starts at about 400 K and has finished at 500 K. Hence, this carbon species is very active under Fischer–Tropsch conditions. The TPH profile of the 20Ni/TiO_2 catalyst is rather similar to the TPH pattern of the 20Ni/SiO_2 catalyst. However, the total amount of deposited carbon is lower for 20Ni/TiO_2. Only a very small amount of carbon is hydrogenated above 500 K. The TPH profile of 2Ni/TiO_2 deviates significantly from those of 20Ni/SiO_2 and 20Ni/TiO_2. The hydrogenation starts at about 400 K and the curve shows the presence of at least three different types of carbon. The hydrogenation of the most stable carbon is only achieved at 660 K. The first type of carbon is probably the same as the carbon present in the 20Ni/SiO_2 and 20Ni/TiO_2 catalysts. The hydrogenation of the second type of carbon sets in at about 500 K and the hydrogenation of the third kind of carbon shows a peak maximum at about 575 K. These carbon species present within the 2Ni/TiO_2 catalyst are less active toward hydrogen than the carbon species present within 20Ni/SiO_2 and 20Ni/TiO_2.

TABLE 4

Amount of Carbon Deposited after 6 h of Fischer–Tropsch Synthesis

Catalyst	mg carbon/ g catalyst	mg carbon/ g nickel	mole carbon/ mole nickel
20Ni/SiO_2	3.2	16	0.08
20Ni/TiO_2	1.4	7	0.03
20Ni/TiO_2^*	2.2	11	0.05
2Ni/TiO_2	4.7	235	1.15

Note. Catalysts were reduced at 673 K, except 20Ni/TiO_2^*, which was reduced at 773 K.

In Fig. 12 the TPH profiles after Fischer–Tropsch synthesis are presented for 20Ni/TiO_2 catalysts which were previously reduced at 673 and 773 K. The TPH pattern has changed when the reduction temperature is raised. After reduction at 773 K the amount of carbon which can be hydrogenated below 500 K has become less, and the amount of the carbon species which can be hydrogenated above 500 K has increased.

The magnetic measurement and the TPH experiment of the 20Ni/TiO_2 catalyst agree very well. Magnetic measurements show that during Fischer–Tropsch synthesis part of the nickel phase (either the surface of all particles or the bulk of some particles) is carbided. The TPH experiment points to a carbon/nickel mole fraction of 0.03, also indicating that only part of the nickel has reacted to a nickel carbide (Table 4). Furthermore, both types of experiment show that the hydrogenation of the deposited carbon species already takes place below 500 K. This type of carbon (α'-carbon) is

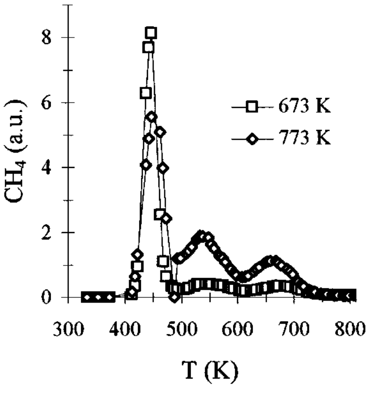

FIG. 12. Temperature-programmed hydrogenation experiments of 20Ni/TiO_2 after reduction at 673 or 773 K and Fischer–Tropsch synthesis at 525 K.

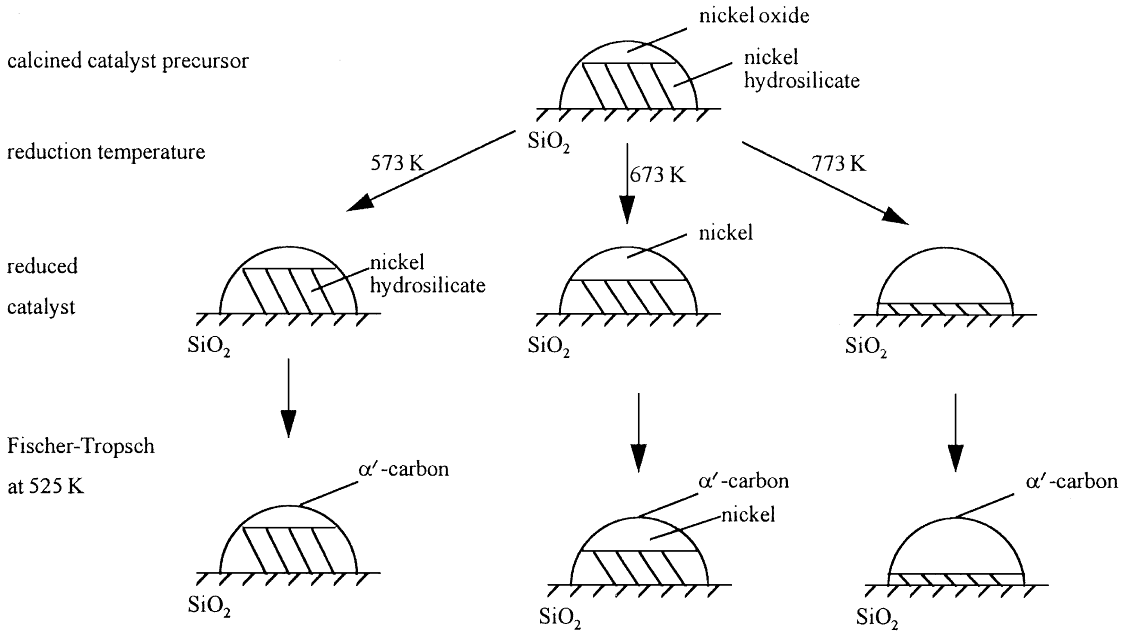

FIG. 13. A model for the nickel on silica system.

most probably involved in the formation of methane as can be concluded from the selectivities of the Fischer–Tropsch measurements (Tables 2 and 3).

During Fischer–Tropsch synthesis over 2Ni/TiO$_2$ the magnetization disappears almost completely, probably due to the formation of nickel carbide. The carbon/nickel mole fraction of 1.15 after Fischer–Tropsch synthesis also indicates that the active nickel phase can be converted to a nickel carbide. Furthermore, the hydrogenation of the second and the third types of carbon (α-carbon) between 500 and 660 K, as was measured with TPH, is in agreement with the results of the magnetic measurements, showing that metallic nickel is formed above 600 K. These types of carbon are probably related to the production of higher hydrocarbons under Fischer–Tropsch conditions, whereas carbon which is hydrogenated below 500 K is involved in the formation of methane. Thus for the production of higher hydrocarbons α-carbon species have to be present on the surface of the active phase. This is in agreement with the experiments with 20Ni/SiO$_2$, which show only α'-carbon species, while in the Fischer–Tropsch experiments mainly methane was observed.

This explanation is confirmed by the TPH experiments performed with the 20Ni/TiO$_2$ catalyst after two different reduction procedures before Fischer–Tropsch synthesis (Fig. 12). After the reduction treatment at 773 K also α'-carbon species are present and this catalyst shows in the Fischer–Tropsch synthesis the formation of higher hydrocarbons. After reduction at 673 K almost exclusively α-carbon species are present and in the Fischer–Tropsch synthesis mainly methane was observed.

Models for the Silica-Supported and Titania-Supported Nickel Catalysts

From the experimental results described and discussed above, models are now deduced to visualize the nature of the silica-supported and titania-supported nickel catalysts. The proposed models are represented in Figs. 13 and 14.

After each reduction temperature the silica-supported catalysts contain metallic nickel particles and only the degree of reduction varies with the reduction temperature (Fig. 13). Therefore, the silica-supported catalysts can be described as metallic nickel particles present on an inert silica support. The hydrogen dissociation is very fast on the surfaces of the nickel particles and carbon and oxygen atoms formed by the dissociation of CO react immediately with hydrogen to form methane and water. Therefore, only very reactive α'-carbon is present at the surface of these nickel catalysts.

The high-loaded titania-supported catalyst (20Ni/TiO$_2$) shows after reduction at 573 and 673 K mainly methane production, whereas after reduction at 773 K also a large amount of higher hydrocarbons is observed. This can be explained by the fact that during the reduction procedure titania can be reduced to TiO$_x$ ($x < 2$) species (Fig. 14). These TiO$_x$ species are mobile and can cover part of the nickel surface (14, 15). The CO and H$_2$ adsorption and dissociation properties, are changed by the presence of TiO$_x$. The H$_2$ adsorption capacity is decreased by the presence of TiO$_x$ on the nickel surface (2). The dissociation of CO, on the other hand, is promoted, probably by a joint action of the carbon-accepting nickel surface and the oxygen-accepting

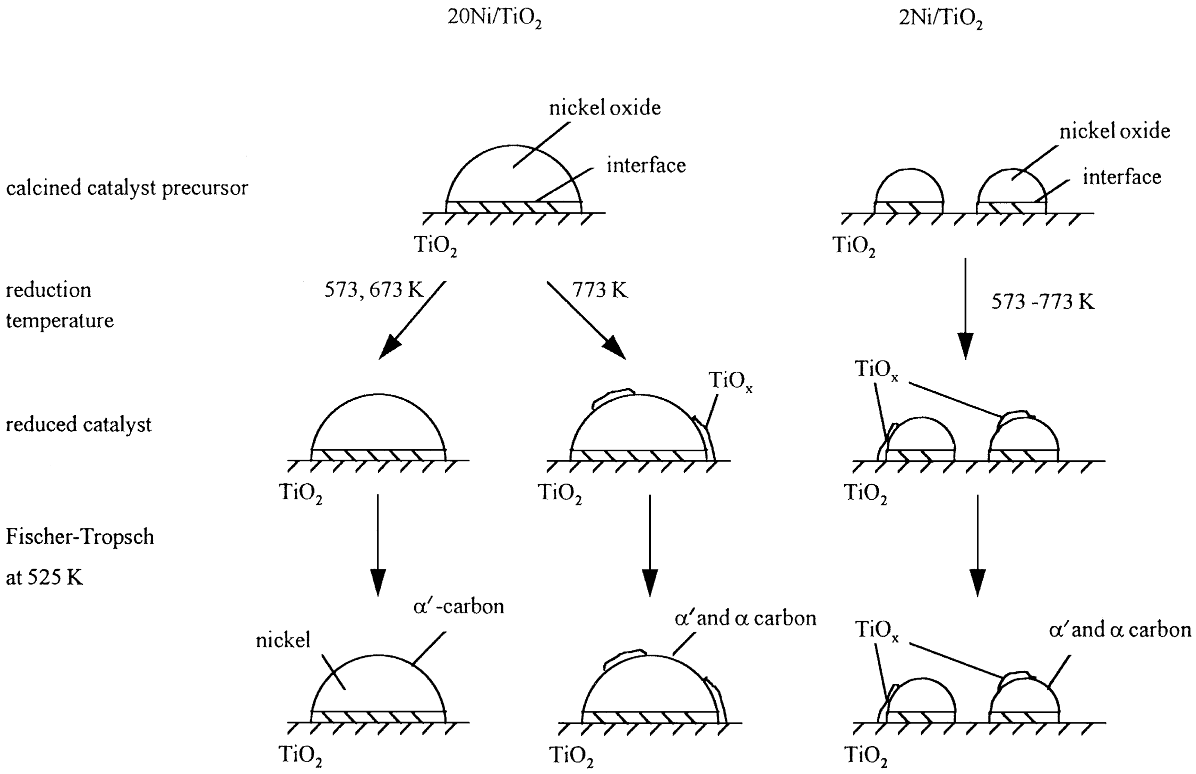

FIG. 14. A model for the nickel on titania system.

TiO$_x$ species (1, 16). Burch and Flambard (17) also propose a unique catalytic site, on which the CO dissociation takes place, to explain the enhanced CO dissociation. The increased amount of active carbon at the surface together with the decreased amount of dissociated hydrogen leads to the formation of α-carbon, probably out of α'-carbon, and subsequently to the production of higher hydrocarbons. It was also shown by Mirodatos *et al.* (18), who studied the influence of alkali promoters on Ni/SiO$_2$ catalysts, that when the CO dissociation is enhanced the amount of carbon present in the catalyst is increased and the selectivity toward higher hydrocarbons is also increased. In their case the weakening of the CO bond was caused by the presence of sodium, whereas in our system this most probably due to the effect of the TiO$_x$ species. The oxygen uptake of TiO$_x$ indicates that the nickel–TiO$_x$ contact perimeter may be important for the production of higher hydrocarbons. Furthermore, the TiO$_x$ species, which are a prerequisite with this explanation, have to be stable during Fischer–Tropsch synthesis. Under reaction conditions H$_2$O is also present, which can oxidize TiO$_x$ to TiO$_2$. Tauster *et al.* (2) reported that at least some of the TiO$_x$ species remain present at high temperature in a H$_2$/CO/H$_2$O atmosphere. The remaining TiO$_x$ species can cause effects as described above. During Fischer–Tropsch synthesis, in addition to α'-carbon, α-carbon is also present on the nickel surface. This type of carbon is most likely to lead to the production of higher hydrocarbons and is responsible for the deactivation with time on stream.

The low-loaded titania-supported catalyst (2Ni/TiO$_2$) produces after each reduction procedure higher hydrocarbons. Apparently, TiO$_x$ species are already present on the nickel surface after reduction at a relatively low temperature (573 K) or the nickel particles in 2Ni/TiO$_2$ are very small and, consequently, a significant fraction of the nickel surface atoms are already in contact with the titania support. Thus, the CO and hydrogen dissociation properties are already changed by TiO$_x$ species after reduction at relatively low temperatures causing the presence of α'- and α-carbon on the active nickel surface and hence the production of higher hydrocarbons. The increase in the selectivity toward higher hydrocarbons, comparing TiO$_2$-supported nickel and SiO$_2$-supported nickel catalysts, after reduction at relatively low temperature was also observed by Turlier *et al.* (6). Obviously, it is not necessary to use high reduction temperatures, that is, SMSI conditions, to increase the selectivity toward higher hydrocarbons.

CONCLUSIONS

In this study it is shown that silica-supported nickel catalysts show a methanation behavior during Fischer–Tropsch synthesis, that is, a high selectivity toward methane and a constant CO conversion, independent of both the nickel loading and the reduction temperature.

Furthermore, it is found that titania-supported nickel catalysts also show this methanation behavior for highly loaded catalysts reduced at relatively low temperatures. However, high-loaded catalysts as well as low-loaded catalysts reduced at high temperatures show the production of high amounts of higher hydrocarbons. This is most probably due to an interaction between nickel and TiO_x ($x < 2$) species, which can cover part of the nickel particles. The TiO_x species promote the CO dissociation and decrease the hydrogen dissociation. The change in dissociation properties can probably cause the change in the product selectivity and the different types of carbon present at the surface.

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