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Conversion of activated carbon into porous silicon carbide by fluidized bed chemical vapour deposition*

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ABSTRACT

A new preparation method is described to synthesize porous silicon carbide. It comprises the catalytic conversion of preformed activated carbon (extrudates or granulates) by reacting it with hydrogen and silicon tetrachloride. The influence of crucial conversion parameters on support properties is discussed for the SiC synthesis in a fixed bed and fluidized bed chemical vapour deposition reactor. The surface area of the obtained SiC ranges from 30 to 80 m^2/g. The metal support interaction (MSI) and metal support stability (MSS) of Ni/SiC catalysts are compared with that of conventional catalyst supports by temperature programmed reduction. It is shown that a Ni/SiC catalyst shows a considerable lower MSI than Ni/SiO_2- and Ni/Al_2O_3-catalysts. A substantially improved MSS is observed; an easily reducible nickel species is retained on the SiC surface after calcination at 1273 K.

1. INTRODUCTION

During the last two decades much effort has been devoted to the development of ceramic, non-oxidic, and non-metallic catalysts [1-3]. This class of materials consists mainly of carbides, nitrides, and borides of transition metals, and possesses interesting properties regarding their catalytic activity and thermal stability. However, the difficulty in controlling the surface composition during synthesis and application of these materials have limited their use at commercial scale. Research for the development of ceramic non-oxidic catalyst supports has mainly been focused on silicon carbide. The physical properties of bulk SiC (high thermal stability, resistance against oxidation, hardness, and inertness of its surface) suggest that it is a promising candidate for catalytic operations at high temperatures or liquid phase reactions at demanding pH conditions. Several ways are reported to synthesize high surface area SiC powder. Examples are gas phase decomposition of $Si(CH_3)_4$ at 1773 K to obtain SiC powder with surface areas near 50 m^2/g [4], reaction of gaseous SiO and activated carbon to form SiC of 59 m^2/g [5], and pyrolysis of organosilicon gels to arrive at SiC of

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179 m^2/g [6]. A limited amount of data is reported which compares the properties of SiC based catalysts with those of conventional catalyst supports. Because all reported preparation procedures of porous SiC are expected to be much more expensive than those of SiO_2 and Al_2O_3, utilization of SiC has to provide substantial advantages over conventional supports to make its production economically attractive. Properties of SiC, which are expected to allow an improved performance compared with SiO_2 and Al_2O_3, are high thermal stability, stability under demanding pH conditions, and weak metal support interaction. In practice, this means that application of SiC as catalyst support will be in processes which benefit considerably from these particular properties. This paper reports on the results of the conversion of preformed activated carbon such as extrudates and granulates, utilizing a fixed bed and fluidized bed reactor for reacting activated carbon with hydrogen and silicon tetrachloride ($SiCl_4$). To achieve a substantial carbon conversion the use of an additional catalyst is essential [7]. Thus, the reactivity of the carbon is enhanced owing to the gasification activity of the catalyst. Research has shown that nickel is appropriate for catalyzing both the gasification and SiC formation. The overall reaction of carbon, hydrogen, and silicon tetrachloride to silicon carbide and hydrogen chloride can be separated into reaction 1 and 2.

$$C(s) + 2H_2(g) \overset{Ni}{\rightleftharpoons} CH_4(g) \quad (1)$$

$$SiCl_4(g) + CH_4(g) \overset{Ni}{\rightleftharpoons} SiC(s) + 4HCl(g) \quad (2)$$

The influence of crucial synthesis parameters on the conversion and characteristics of this support material has been investigated. Especially the stability of the catalyst at elevated temperatures is of primary importance. To discriminate between differences in catalytic behaviour originating from a pure metal support interaction and reaction of the support with the active phase, the expression "metal support stability" (MSS) is introduced. Both the MSI and MSS are investigated for the Ni/SiC catalyst and are compared to nickel catalysts based on conventional supports (SiO_2 and Al_2O_3).

2. EXPERIMENTAL

This section deals with the methods of preparation of porous SiC and SiO_2, Al_2O_3 and SiC based catalysts. Physical properties of the applied supports are shown in Table 1.

2.1. Preparation of high surface area SiC

Activated carbon extrudates (Norit RW08) are impregnated with nickel by the incipient wetness method ($Ni(NO_3)_2 \cdot 6H_2O$ in water) to arrive at nickel contents of 2, 5, or 8 w%. After drying overnight at 385 K the extrudates are placed as a fixed bed (length 1 mm) in a tubular quartz reactor (internal diameter 42 mm). The reactor is heated (0.167 K/s) under flowing hydrogen at 100 kPa to 1400 K and maintained at this temperature for 5 minutes. Subsequently, the reactor was cooled down to the desired reaction temperature. The concomitant weight decrease for 2w% Ni/C due to gasification amounts to 18 %. The hydrogen flow is subsequently increased to 3.69 mol/h, the pressure is adjusted to 10 kPa and

Table 1
Physical properties of catalyst supports

Support	Code	S_{BET} (m^2/g)	V_{pore} (ml/g)	Geometry
Activated carbon extr.	Norit RW08	947	1	3 mm × 0.8 mm
Activated carbon gran.	Norit Elorit	655	0.6	d_{50}:450μm
SiO_2	Engelhard Si-162-1	30	0.6	grinded extr.
Al_2O_3	Engelhard Al-4196	8	0.6	grinded extr.

extr.: extrudate, gran.:granulate

gaseous silicon tetrachloride ($SiCl_4$) is introduced (flow rate 0.14 mol/h). After reaction the reactor is pressurized to 100 kPa and cooled down under flowing hydrogen to room temperature.

Nickel loaded activated carbon granulates (Norit Elorit) are prepared using the incipient wetness method ($Ni(NO_3)_2 \cdot 6H_2O$ in water) to arrive at 5 w% and followed by drying overnight at 385 K. The conversion is carried out in a fluidized bed chemical vapour deposition (FB-CVD) reactor of which the set-up is displayed in Figure 1.

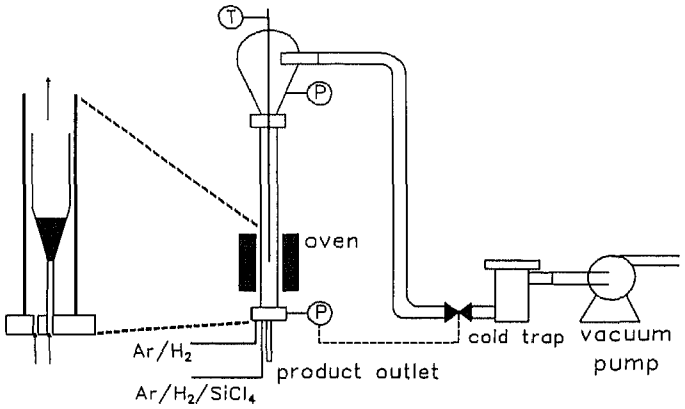

Figure 1. Schematic drawing of the Fluidized Bed CVD reactor

The enlarged part represents the cone shaped quartz reactor (cone angle 7°, length 0.15 m) inside an alumina tube. The gas flow rate at the cone entrance (internal diameter 2.7 mm) exceeds the velocity of entrainment of the particles. Low pressure operations are frequently necessary for CVD reactions. Sub-atmospheric pressure control is achieved by incorporation of a vacuum pump, cold trap, and a butterfly valve downstream of the reactor. The conversion procedure starts by filling the reactor with 3 g activated carbon (5w% nickel) under flowing argon (2.46 mol/h). Air is removed by decreasing the pressure and flow rate in steps to 10 kPa and 0.246 mol/h, respectively, followed by restoring the initial pressure and flow rate. This procedure is repeated three times, followed by heating to 1380 K. At this

point the reaction is started by replacing part of the argon by hydrogen and $SiCl_4$.

2.2. Characterization of porous SiC

X-ray Diffraction (Philips Powder Diffractometer PW1840, CuKα) has been used to detect the crystalline products in the material. The morphology of the porous SiC has been investigated by Scanning Electron Microscopy (JEOL JSM-35, 15 to 20 kV); the substrates were coated with gold or platinum to suppress charging. Thermal Gravimetric Analysis (Stanton Redcraft STA-1500) has been used to determine the carbon conversion. A sample of 20 mg is heated by 0.167 K/s in air to 1273 K, the weight decrease and heat flux are simultaneously recorded.

2.3. Testing of SiC based catalysts

Removal of the residual carbon present in the SiC/C mixture after conversion is carried out by oxidation in dry air (1023 K, 4h). The SiC resulting from the 5w% Ni/C will be referred to as SiC-5. Catalyst preparation for TPR consisted of loading Ni on SiO_2, Al_2O_3, and SiC-5 by the incipient wetness method to arrive at a 5w% metal content. After impregnation the catalysts were dried at 353 K overnight and calcined at 773 K and 1273 K for 8 hours. Temperature programmed reduction was carried out with a 2:1 hydrogen-argon mixture (total flow rate 0.5 ml/s) and a heating rate of 0.167 K/s. The hydrogen consumption and hydrocarbon production was analyzed with a TCD and FID respectively. Typically 100 to 400 mg sample was used. The thermal and hydrothermal stability were evaluated according to a method described by Lednor and de Ruiter [8]; SiC-5 was aged at 1273 K under flowing nitrogen; the hydrothermal stability was determined at 1023 K and 1273 K under flowing nitrogen containing 2v% H_2O.

3. RESULTS AND DISCUSSION

3.1. Conversion of activated carbon extrudates

The optimal temperature for SiC formation has been determined by performing experiments at 1075, 1250, and 1378 K and utilizing 2w% Ni on carbon. The results of XRD analysis of the products are displayed in Figure 2. At low temperatures (1075 K) mainly silicon is formed by reaction 3.

$$SiCl_4(g) + 2H_2(g) \rightleftharpoons Si(s) + 4HCl(g) \quad (3)$$

Silicon deposition is encountered in similar experiments in the absence of a catalyst at 800 to 1400 K. Increasing the temperature leads to silicon carbide formation, which is most pronounced at the highest temperature, *i.e.* 1378 K. The enhancement in SiC formation originates from at least one catalytic effect of nickel, *i.e.* gasification of the carbon according to reaction 1. Research by Moene *et al.* [9] showed that the reaction between activated carbon and $SiCl_4$ is limited below 1450 K. Vincent *et al.* [10] reported that a considerable non-catalytic conversion of graphite powder into SiC according to reaction 4 necessitates temperatures above 1600 K.

$$SiCl_4(g) + 2H_2(g) + C(s) \rightleftharpoons SiC(s) + 4HCl(g) \quad (4)$$

Conventional CVD of SiC usually comprises decomposition of CH_3SiCl_3, although numerous reports display the possibilities of using separate carbon and silicon sources [11], *e.g.* SiH_4/C_3H_8 and $SiCl_4/CH_4$. Utilizing CH_3SiCl_3 the deposition temperature can be as low as 1173 K, which is the result of the formation of gas phase radicals by decomposition of the Si-C bond in the CH_3SiCl_3 molecule. The temperature required for stoichiometric SiC formation from separate C and Si sources is generally higher (above 1373 K). Extensive SiC deposition at 1378 K (Figure 2) points to the presence of gaseous carbon precursors during the synthesis reaction.

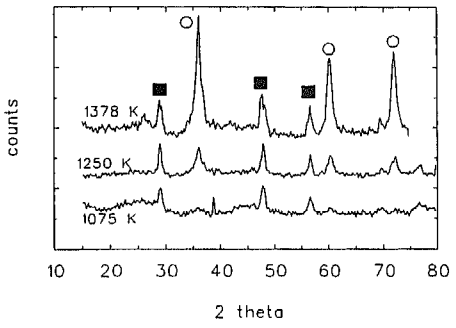

Figure 2. XRD profiles of converted extrudates 2w% Ni/C, 1 h reaction
○:SiC, ■:Si

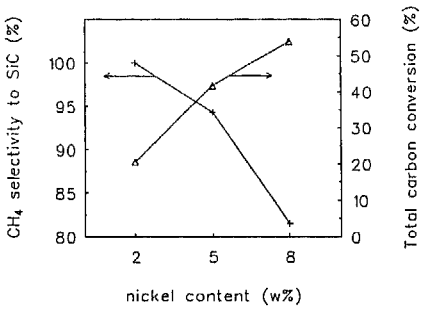

Figure 3. CH_4 selectivity to SiC formation (+) and total carbon conversion (△) as a function of nickel content (1 h reaction, extrudates)

Of course, it is essential to deposit SiC without Si formation. This means that sufficient methane has to be formed by gasification in order to eliminate Si formation. The amount of CH_4 and SiC formed during reaction can be determined utilizing TGA in combination with a silicon and carbon mass balance. The results of these calculations are shown in Figure 3. Identical reaction rates for CH_4 and SiC formation are found for a nickel content of 2w%, which is shown in Figure 3 as a 100% CH_4 utilization for SiC formation. The corresponding total carbon conversion equals 22%. Increasing the amount of nickel results in higher carbon conversions and a concomitant decrease in CH_4 selectivity. Mass transfer calculations show that this decline originates from diffusion limitations of $SiCl_4$ inside the carbon extrudate.

3.2. Conversion of activated carbon granulates

Activated carbon granulates are converted in the FB-CVD reactor. TGA analysis has been used to calculate the composition of the granulates after conversion and carbon removal. These compositions and the specific surface areas are shown in Table 2. The amount of ash originates from the activated carbon and the nickel applied. Owing to a concomitant increase in carbon conversion by utilizing increased amounts of nickel, the relative nickel content remains almost constant. Prior to oxidation the surface area is determined by a combination of the original carbon and the SiC. Removal of the carbon discloses the textural properties of the SiC; the surface areas vary between 30 and 80 m^2/g, which is sufficient for catalytic purposes, especially at high temperatures reactions (> 1000 K).

Table 2
Composition and specific surface area of converted activated carbon extrudates

	2w% Ni		5w% Ni		8w% Ni	
SiC (w%)	36	(82)	54	(85)	57	(82)
C (w%)	56	(0)	36	(0)	32	(0)
ash (w%)	8	(18)	10	(15)	11	(18)
S_{BET} (m^2/g)	300	(80)	206	(31)	137	(34)

Values in brackets: properties of the extrudates after removal of residual carbon by oxidation

3.3. Testing of SiC based catalysts

The TPR profiles of nickel catalysts are depicted in Figures 4 to 6.

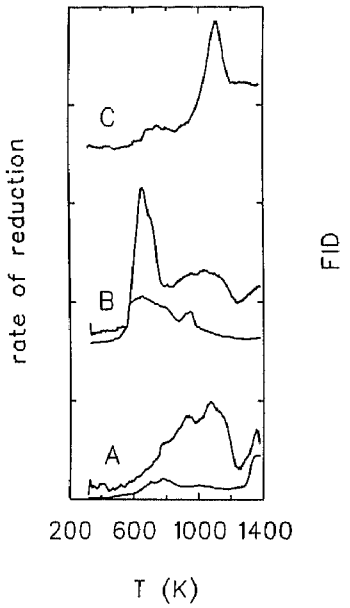

Figure 4. TPR profiles of SiO_2 (A), 5w% Ni/SiO_2 calcined at 773 K (B) and 1273 K (C). Both the TCD and FID signal are displayed (upper and lower curve, respectively)

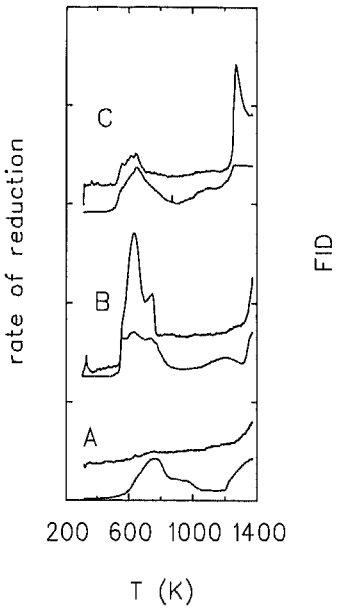

Figure 5. TPR profiles of Al_2O_3 (A), 5w% Ni/Al_2O_3, calcined at 773 K (B) and 1273 K (C). Both the TCD and FID signal are displayed (upper and lower curve, respectively)

The silica contains sulfate which produces a broad peak from 600 to 1200 K (Fig. 4^A). The TPR profile of a 5w% Ni/SiO_2 catalyst calcined at 773 K for 8 hours is in agreement with literature [12,13]. Calcination at 1273 K leads to a considerable increase of the temperature

at the maximum reduction rate (T_{max}), *viz.* from 655 K to 1110 K. A similar trend is observed for the alumina catalysts; an increase of calcination temperature from 773 K to 1273 K corresponds to a shift in the T_{max} from 630 K to 1120 K. Both observations can be explained by solid state reactions of NiO with the support resulting in silicates and aluminates, respectively [14,15]. The TPR profiles of the Ni/SiC-5 catalysts differ considerably compared to those of the conventional supported NiO catalysts.

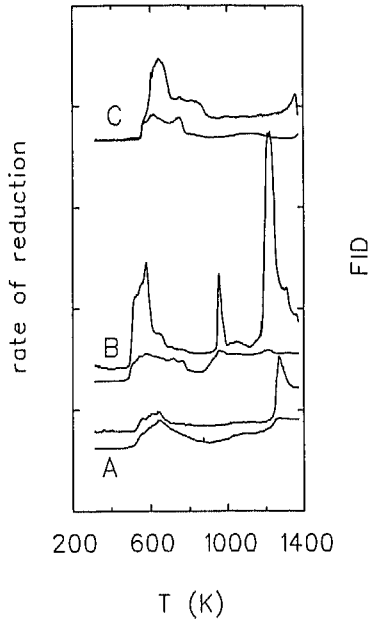

Figure 6. TPR profiles of SiC-5 (A), 5w% Ni/SiC-5 calcined at 773 K (B), and 1273 K (C). Both the TCD and FID signal are displayed (upper and lower curve respectively)

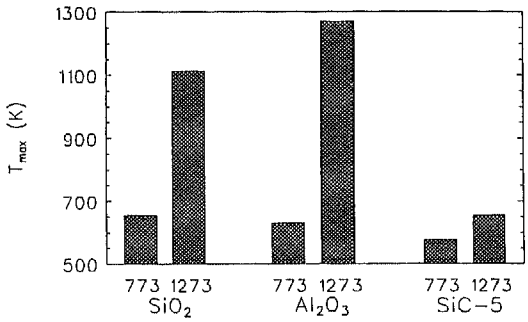

Figure 7. Temperature at the maximum rate of reduction for nickel catalysts (5w% Ni on SiO_2, Al_2O_3, and SiC-5) calcined at 773 K and 1273 K

It is shown in Figure 6 that part of the nickel oxide, applied in the carbon conversion, reduces around 600 K. Calcination of the Ni/SiC-5 catalyst at 773 K results in an easily reducible nickel oxide species as is shown by the low T_{max} (575 K). After the formation of metallic nickel a second, sharp, peak arises at elevated temperatures (955 K) and the FID signal increases. This probably originates from the formation of Ni_3Si and a carbon phase according to reaction 5.

$$3Ni(s) + SiC(s) \rightleftharpoons Ni_3Si(s) + C(s) \qquad (5)$$

Similar solid state reactions are reported by Chou *et al.* [16], who reported extensive

decomposition of SiC at temperatures exceeding 1370 K. The peak at 955 K can be rationalized by considering the intimate contact of the catalyst system which decreases the temperature at which the first SiC layer reacts with nickel. The solid carbon gasifies into methane at 955 K, at 1220 K this reaction accelerates and starts to consume the SiC considerably. The most remarkable feature of the Ni/SiC-5 system is, however, its behaviour after calcination at 1273 K for 8 hours. Nickel oxide reduction occurs in a broad region of which the T_{max} (640 K) is similar to that of Ni/SiO_2 and Ni/Al_2O_3 catalysts calcined at 773 K. This points to a remarkably low metal support interaction and a high metal support stability. Surface oxidation of SiC is to be expected during calcination at 1273 K. This Si-O layer, however, does not correspond to bulk silica as is shown by the differences in reduction temperatures of NiO. The broad shoulder appearing in the reduction peak of profile 6^C in the temperature range of 700 to 900 K suggests the presence of nickel silicates [12]. The oxidic layer probably prevents reaction of metallic nickel with the underlying silicon carbide up to temperatures of 1373 K. Figure 8 shows that a complete reduction of NiO is achieved below 700 K for all catalysts after calcination at 773 K.

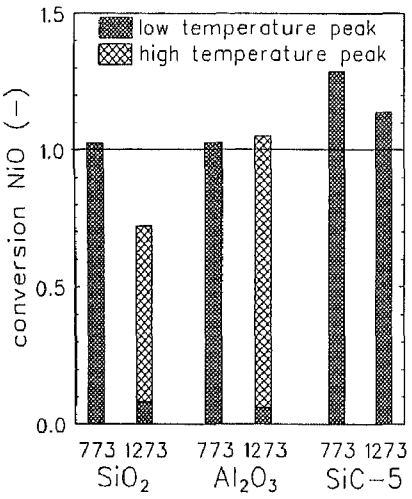

Figure 8. Conversion of NiO on SiO_2, Al_2O_3, and SiC-5 (5w% metal content) calcined at 773 and 1273 K, calculated from the total hydrogen consumption, 1000 K is used to distinguish a low and high temperature region

The amount of nickel oxide reduced in the high temperature region (above 1000 K) relative to the total reduced amount NiO, increases to over 90 % for the silica and alumina based catalysts calcined at 1273 K. Complete reduction of NiO is achieved in the low temperature region for the SiC based catalyst calcined at 1273 K. The presence of Ni_2O_3 can rationalize the more than stoichiometric hydrogen consumption of the Ni/SiC catalyst. High temperature calcination decreases the maximum reducible NiO amount for the SiO_2 catalyst to 72%. Although some difficulties are encountered in integrating the reduction peak owing to the presence of sulfur in the SiO_2, this may point once more to a significant difference between

the interaction of NiO on partially oxidized SiC and on SiO_2.

Finally, the stability of SiC-5 at 1273 K in nitrogen and at 1023 K in a nitrogen-steam mixture is very good, no sintering of the porous structure is observed. However, exposing SiC at 1273 K to 2v% steam in nitrogen results in a considerable decrease in specific surface area, *i.e.* from 31 to 19 m^2/g. Part of this decrease (from 31 to 26 m^2/g) originates from a weight increase owing to surface oxidation of the SiC-5.

4. CONCLUSIONS

Preformed activated carbon, such as extrudates and granulates, can be converted into porous SiC. The presence of nickel on the activated carbon is essential for catalyzing the gasification by hydrogen and subsequent reaction of methane with silicon tetrachloride into SiC. This procedure results in SiC with surface areas of 30 to 80 m^2/g. TPR analyses of 5w% Ni/SiC catalysts disclose a remarkably low metal support interaction compared to nickel catalysts based on conventional supports. The SiC based catalysts aged at 1273 K in air show a metal support stability which is substantially higher than that of Ni/SiO_2 and Ni/Al_2O_3 catalysts. The thermal stability in non-oxidizing environments is very good, which permits utilization of this catalyst at elevated temperatures. The areas, in which SiC is applicable, are restricted; complete oxidation of SiC has to be avoided. It can be concluded that this Ni/SiC system can be exposed to high temperatures (above 1100 K) in reducing environments, in which metallic nickel maintains its catalytic activity. Application of this system at these conditions will probably provide substantial advantages over nickel catalysts based on SiO_2 and Al_2O_3.

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