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Novel application of catalysis in the synthesis of catalysts

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A novel method has been developed for the synthesis of catalysts applying chemical vapour deposition techniques. It comprises the catalytic conversion of a porous solid which acts as a reactant and a template. The catalyst increases the reactivity of the solid and enhances the rate of formation of the desired product. The results of applying this method for the synthesis of high surface area SiC will be highlighted. Activated carbon equipped with nickel is converted into SiC by reaction with hydrogen and silicon tetrachloride at 1380 K. Nickel catalyzes both the gasification ($C(s) + 2H_2(g) \rightarrow CH_4(g)$) and the SiC formation via the CVD reaction: $SiCl_4(g) + CH_4(g) \rightarrow SiC(s) + 4HCl(g)$. Thus porous SiC is obtained with the same shape of the original activated carbon (extrudate) and possesses surface areas up to 80 m^2/g.

Keywords: catalyst manufacture; chemical vapour deposition (CVD); high surface area silicon carbide; activated carbon

1. Introduction

Conventional catalyst preparation comprises the application of catalytically active material onto pre-shaped supports. "Wet" methods are most frequently employed and consist of contacting the support with a solution which contains the desired metals. Subsequent drying, calcination, and reduction provide the catalyst. Gas-phase methods, e.g. chemical vapour deposition, for metal deposition onto SiO_2 and Al_2O_3 have been reported in literature as a promising technique for catalyst design [1–3]. We feel that the use of this technique will expand in the near future, owing to the inherent higher process flexibility, ease of scale-up and tailoring of the active-site distribution in the catalyst support by proper selection of deposition conditions [3]. Moreover, CVD can alleviate the difficulties concerning regeneration of structured catalytic convertors, like monolithic reactors, because the rejuvenation is then allowed to be carried out in situ.

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Today gas-phase techniques play an important role in the development of new non-oxidic catalysts. These catalysts, which usually consist of transition metal carbides and nitrides, are found to exhibit behaviour which resembles that of noble metal catalysts (e.g. Pt, Pd, Ru) [5]. Four types of reactions have been explored for the synthesis of high area carbides and nitrides [6], solid-state, gas–solid, gas-phase, and solution-phase reactions. We report on a novel class of reactions which embodies both the merits of gas–solid and gas-phase reactions.

1.1. THE CONCEPT OF CATALYST (SUPPORT) PREPARATION UTILIZING A POROUS SOLID AS REACTANT AND TEMPLATE

The starting point is a porous solid which has been loaded with a suitable catalyst. A mixture of reacting gases are subsequently admitted which (1) gasify the solid and (2) react with the gasification products to form the desired material. Fig. 1 displays the mechanism. Both reactions are catalyzed, which is pictured by the shaded spherical halves. Moreover, the solid will thus act as a reactant as well as a template for the deposition of the material. As a consequence, the initial external morphology determines the final structure of the product, while the final textural properties are governed by the pore structure of the original solid. The conversion of a macroscopic scale resembles that of a gas–solid reaction with its inherent experimental simplicity, whereas on a microscopic level adsorbed gaseous molecules react to form the desired product. Hence, obvious difficulties in gas–solid reactions regarding diffusion through the developed product layer are elegantly overcome. To the best of our knowledge this concept of a dual catalytic action and dual utilization of the solid is new.

In general, a high surface area carbon substrate is the primary substrate to be catalytically converted. The gas mixture then contains hydrogen as gasifying species; the product methane is subsequently converted with another gaseous component into the preferred ceramic. Instances of potential carbides formed are SiC, B_xC_y, TiC, Mo_2C, WC, and W_2C. Although the main use of this conversion method lays in the formation of carbidic ceramics (owing to the ease of gasification of carbon) other systems can be feasible as well. Using porous silicon or titanium as solid source, gasification can easily be carried out with Cl_2, which opens possibilities for the synthesis of porous ceramics, like Si_3N_4, TiC, and TiN.

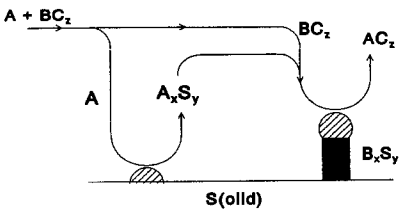

Fig. 1. The mechanism of catalyzed solid conversion for the synthesis of catalysts.

1.2. APPLICATION OF THE REACTANT/TEMPLATE CONCEPT IN THE SYNTHESIS OF HIGH SURFACE AREA SILICON CARBIDE

High surface area silicon carbide (>20 m^2/g [6]) is one of the most promising non-oxidic catalyst supports for applications at high temperatures owing to its inertness, high thermal stability and high thermal conductivity. Porous SiC of 50 m^2/g has been synthesized by Vannice et al. [7] via gas-phase decomposition of $Si(CH_3)_4$ at temperatures around 1700 K. Shaping of the powder into manageable forms, however, is expected to be laborious owing to the low sinterability of SiC. A gas–solid reaction of SiO and activated carbon has been investigated by Ledoux and co-workers [8] attaining surface areas of 59 m^2/g. It was mentioned that the material synthesized probably consists of a skeleton of carbon covered by a protective coating of SiC, indicating that diffusional limitations of SiO through the SiC product layer limit the (rate of) conversion of the carbon.

The drawbacks of both methods can be overcome by utilizing the concept of catalyzed conversion as described above. The experimental procedure of the reactant/template concept will be given below.

2. Experimental

The physical properties of the applied Norit activated carbons are given in table 1. The Azo carbon is sieved to obtain particles in the range of 63 to 180 μm and used without further pretreatment. The Elorit granulates are pre-fluidized for 3 h to remove the fines and decrease the initial attrition of the carbon. A sieve fraction with a diameter of 300–425 μm has been selected for conversion. In some cases this fraction has previously been subjected to an alkaline and acid washing procedure. This washing procedure resulted in a decrease in ash content from 8 to 5 wt%. Nickel nitrate hexahydrate (>99%) and silicon tetrachloride (>98%), both from Janssen Chemica, were used. Activated carbon granulates were loaded with nickel by pure volume impregnation of the carbon with a solution of $Ni(NO_3)_2 \cdot 6H_2O$ in demineralized water to arrive at nickel contents of 2, 5, or 8 wt% nickel. Drying was performed at atmospheric pressure in air at 385 K. The gases used for carbon conversion, argon and hydrogen, were purified by passing them over a Cu/Al_2O_3 or Pd/Al_2O_3 catalyst, respectively, followed by drying by molecular sieve 5A.

Table 1
The physical properties of the activated carbon granulates

Carbon	S_{BET} (m^2/g)	V_{pore} (ml/g)	S_t (m^2/g)	V_{micro} (ml/g)	ρ(Hg) (kg/m^3)	ρ(He) (kg/m^3)	Ash (%)
Azo	703	0.88	219	0.23	690	2100	6.9
Elorit	655	0.6	149	0.25	600	2100	8

Conversion of activated carbon extrudates. A schematic picture of the CVD apparatus is shown in fig. 2. The carbon is fluidized in the cone-shaped quartz reactor (entrance diameter: 2.7 mm, cone angle 7°, cone length 140 mm) surrounded by an alumina tube. The gas velocity at the cone entrance exceeds the rate of entrainment of the carbon, whereas the velocity in the upper part of the bed surpasses the minimal fluidization velocity. The pressure is regulated by a pressure transducer at the cone entrance and a butterfly valve in combination with a vacuum pump downstream of the system, which allows CVD experiments to be carried out at subatmospheric pressures. The reactor is loaded with activated carbon (typically 3 to 5 gram) under flowing argon (16.7 ml/s). Subsequently the reactor is evacuated twice to 10 kPa to remove oxygen while the flow rate is simultaneously decreased in steps to 2.5 ml/s to prevent entrainment of the particles out of the reactor. The reactor is heated under flowing argon to 1380 K at 100 kPa during which the nickel nitrate decomposes and the formed nickel oxide is carbo-thermically reduced to metallic nickel. The argon flow is subsequently lowered and hydrogen and silicon tetrachloride were admitted at the proper flow rates; the total flow rate equalled 16.7 ml/s (STP) and the pressure was kept at 100 kPa.

Removal of residual carbon. Residual carbon, present after conversion, has been removed by oxidation in dry air at 1023 K in a tubular reactor.

X-ray diffraction (XRD). X-ray diffractograms were measured with a Philips powder diffractometer (PW1840) using Cu Kα radiation (wavelength 0.154 nm) of the intact extrudates.

Scanning electron microscopy (SEM). The samples were analyzed with a Jeol (JSM-35) scanning electron microscope after sputtering with gold or platinum to determine the morphology of the deposited phases. An acceleration voltage of 15 to 20 keV has been applied.

Thermal gravimetric analysis (TGA). Samples of a size of 20 mg were oxidized in air in a Stanton Redcraft (STA-1500) using a temperature increase of 0.167 K/s from room temperature to 1273 K. Recordings of the weight change and concomitant heat flux were carried out simultaneously.

Surface area measurements. Nitrogen isotherms at 77 K were recorded on a

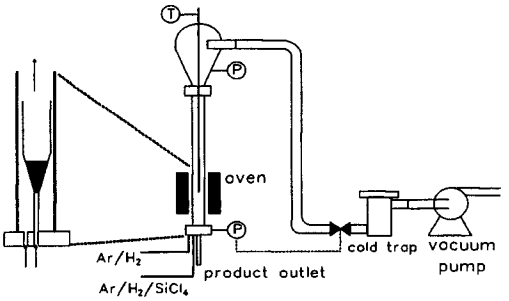

Fig. 2. Scheme of the CVD apparatus.

Carlo Erba Sorptomatic 1800. Prior to measurement the samples were degassed at 423 K and 10^2 Pa. The BET surface area (S_{BET}), t surface area (S_t) and micro pore volume (V_{micro}) were determined.

3. Results

Dual catalytic action of nickel. XRD analysis after conversion demonstrates nicely that the optimal temperature for conversion equals 1380 K as shown by fig. 3. The largest amount of SiC is formed at 1378 K. Some silicon, however, is still present under these conditions. Additional research supplied the crucial parameters which govern the conversion process and enable control of SiC synthesis [9,10]. For instance, silicon co-deposition can be suppressed by applying shorter conversion times or larger amounts of nickel. The indispensability of nickel catalysis is evident for optimal performance when curve a is compared to d. Owing to the gasification activity of nickel solid carbon is transformed into gaseous methane,

$$C(s) + 2H_2(g) \rightarrow CH_4(g) \quad (1)$$

Silicon tetrachloride reacts subsequently with methane to form SiC,

$$SiCl_4(g) + CH_4(g) \rightarrow SiC(s) + 4HCl(g) \quad (2)$$

Nickel catalyzes the second reaction as well which is primarily demonstrated by the abundance of SiC whiskers grown by the vapour–liquid–solid mechanism as shown by SEM analysis. Other evidence can be obtained when the reaction rate of SiC growth is compared with that of non-catalytic CVD grown SiC [11]. In order to allow catalyzed SiC growth via the VLS mechanism the reaction temperature has to surpass 1360 K, permitting the formation of an eutectic Ni-Si-C mixture.

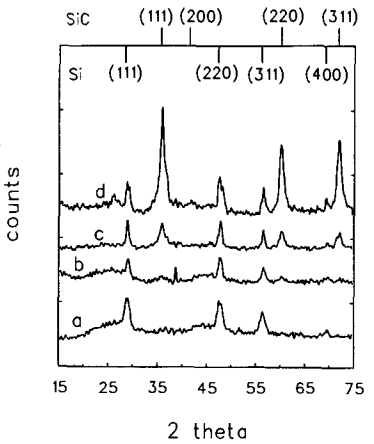

Fig. 3. XRD profiles of converted activated carbon, (a) without Ni-catalysis at 1380 K; (b), (c), and (d) 2 wt% Ni, 1 h reaction, at 1075, 1250 and 1378 K, respectively.

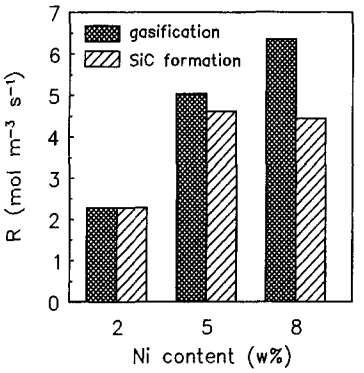

Fig. 4. The rates of gasification and SiC formation (1380 K, 1 h).

Rates of gasification and SiC formation. Thermogravimetric analysis allows the determination of a carbon and silicon mass balance from which the rates of the two reactions can be calculated. Identical rates of gasification are found at a nickel loading of 2 wt%. At higher nickel loadings the SiC formation cannot keep up with the CH_4 formation, which is probably caused by the presence of diffusion limitations of $SiCl_4$, inside the extrudates. It should be mentioned that the conversion product completely consists of SiC in the case of applying 5 and 8 wt% nickel as catalyst.

Shape memory. Removal of the residual carbon is necessary because the carbon conversion is extensive (ranging from 20 to 55%), though not complete. This can be easily achieved by oxidation at 1023 K in air. Total shape memory is secured by this process; the resulting material consists of shaped porous SiC granulates.

Surface area. The specific surface area after conversion (2 wt% Ni, 1380 K, 1 h) equals 200 m^2/g which originates from the SiC and residual carbon, a surface area of 80 m^2/g is retained after oxidation which is high enough for catalytic purposes.

4. Discussion and conclusion

The experiments described above prove the potential of utilizing a catalyst for enhancing the rate of two reactions simultaneously and applying the porous carbon as a reactant as well as a template. Of course the choice of proper catalyst formulation is the least conspicuous step in the entire procedure. Knowledge of gasification catalyst and possible formations of eutectic phases permits, however, a rapid and focused screening of suitable catalysts.

The high surface area silicon carbide formed has high potential as catalyst support in process operating at elevated temperatures. Examples are reforming reactions of methane, generally conducted at temperatures exceeding 1050 K [12,13]. The semiconducting properties of silicon carbide permit the photocatalytic reduc-

tion of CO_2 in aqueous suspensions [14]. The high surface area of the material described above is of major benefit in the optimization of the quantum yield per gram catalyst.

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References

[1] T.J. Thomas, D.A. Hocul and A. Brenner, in: *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, ed. J.S. Miller (American Chemical Society, Washington, 1982) p. 267.
[2] L. Guczi and A. Beck, Polyhedron 7 (1988) 2387.
[3] A.A. Gomenyuk, I.V. Babich, Yu.V. Plyuto and A.A. Chuiko, Russ. J. Phys. Chem. 64 (1990) 891.
[4] R. Moene, M. Makkee and J.A. Moulijn, Chem. Eng. J. 53 (1993) 13.
[5] S.T. Oyama, Catal. Today 15 (1992) 177.
[6] R.W. Chorley and P.W. Lednor, Adv. Mater. 3 (1991) 474.
[7] M.A. Vannice, Y.-L. Chao and R.M. Friedman, Appl. Catal. 20 (1986) 91.
[8] M.J. Ledoux and C. Pham-Huu, Catal. Today 15 (1992) 263.
[9] R. Moene, F.W. Tazelaar, J. Schoonman, M. Makkee and J.A. Moulijn, in: *Proc. Carbon '94*, Granada, Spanish Carbon Group (1994) p. 532.
[10] R. Moene, F.W. Tazelaar, J. Schoonman, M. Makkee and J.A. Moulijn, J. Catal., submitted.
[11] R. Moene, H.Th. Boon, J. Schoonman, M. Makkee and J.A. Moulijn, Carbon, to be submitted.
[12] J.R. Rostrup-Nielsen, in: *Steam Reforming Catalysts* (Teknisk Forlag, Copenhagen, 1975).
[13] A.T. Ashcroft, A.K. Cheetham, M.L.H. Green and P.D.F. Vernon, Nature 352 (1991) 225.
[14] T. Inoue, A. Fujishima, S. Konishi and K. Honda, Nature 277 (1979) 638.