COATING OF ACTIVATED CARBON WITH SILICON
CARBIDE BY CHEMICAL VAPOUR DEPOSITIONR. MOENE,^{a,*} H. TH. BOON,^a J. SCHOONMAN,^b M. MAKKEE,^{a,†} and J. A. MOULIJN^a^aDepartment of Chemical Process Technology, Section Industrial Catalysis, Delft University of
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Abstract—Coating of activated carbon with silicon carbide by chemical vapour deposition (CVD) has been investigated to improve the oxidation resistance and the mechanical strength of activated carbon extrudates. The oxidation resistance has been analyzed by thermal gravimetric analysis in air; the temperature at the maximum rate of oxidation ($T_{\max}$) is used to compare the modified carbons. Selective deposition of SiC by reacting SiCl_4 with the carbon surface cannot be achieved below 1400 K. Silicon deposition has been encountered in all cases. Coating of activated carbon using a $\text{CH}_4/\text{SiCl}_4$ mixture results in SiC deposition at 1376 K. The oxidation resistance of this modified activated carbon has been improved by 150 K ($T_{\max} = 1025$ K), while the side crushing strength improved by a factor 1.7. The residual surface area was $176 \text{ m}^2/\text{g}$. SiC coatings have also been obtained by decomposing CH_3SiCl_3 at temperatures above 1200 K. The side crushing strength of the extrudates improved by a factor of 1.4, while the resistance against oxidation remained similar to that of the original carbon. The residual surface areas and pore volumes averaged $530 \text{ m}^2/\text{g}$ and 0.33 ml/g , respectively. Both methods of SiC deposition result in surface areas which are high enough for catalyst support applications. Evaluation of the infiltration performance of this SiC-CVD process using CH_3SiCl_3 shows that 20–95% of the SiC has been deposited inside the extrudates. The residual porosity of the extrudates is evaluated using a general mathematically developed chemical vapour infiltration design chart, which correlates initial Thiele moduli with the porosity after deposition. Good agreement is obtained between the experimental data and the design chart. Copyright © 1996 Elsevier Science Ltd

Key Words—Activated carbon, modification, chemical vapour deposition, silicon carbide, oxidation resistance, mechanical strength.

1. NOTATION

a	Fitting constant in eqn (6)	S_t	Surface area determined by the t-method ($\text{m}^2 \text{ g}^{-1}$)
ASA	Active surface area	SCS	Side crushing strength (N)
C_p	Heat capacity ($\text{J mol}^{-1} \text{ K}^{-1}$)	$T_{\max}$	Temperature at maximum rate of oxidation during temperature programmed oxidation in air (0.167 K s^{-1})
D_{eff}	Effective diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$)	V_{ext}	Volume of one extrudate
D_{gas}	Diffusion coefficient in the gas phase ($\text{m}^2 \text{ s}^{-1}$)	V_{micro}	Micro pore volume determined by the t-method ($\text{cm}^3 \text{ g}^{-1}$)
D_{Knudsen}	Knudsen diffusion coefficient ($\text{m}^2 \text{ g}^{-1}$)	V_{pore}	Total pore volume ($\text{cm}^3 \text{ g}^{-1}$)
E_a	Activation energy (kJ mol^{-1})	ϵ	Residual porosity
$\Delta_f H$	Heat of formation (J mol^{-1})	ζ	Carbon conversion
k	Reaction rate constant ($\text{mol m}^{-3} \text{ s}^{-1}$)	ϕ	Thiele modulus
k_0	Pre-exponential factor ($\text{mol m}^{-3} \text{ s}^{-1}$)	ρ	Density (kg m^{-3})
L	Characteristic diffusion length (m)	τ	Tortuosity
m	Weight (kg)		
m_0	Initial weight (kg)		
n	Reaction order (—)		
P	Pressure (Pa)		
R	Reaction rate ($\text{mol m}^{-2} \text{ s}^{-1}$)		
S	Absolute entropy ($\text{J mol}^{-1} \text{ K}^{-1}$)		
S_{BET}	Surface area determined by the BET method ($\text{m}^2 \text{ g}^{-1}$)		
S_{ext}	External surface area of one extrudate (m^2)		
S_v	Specific surface area per unit volume		

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2. INTRODUCTION

The use of activated carbon as a catalyst support is mainly limited by its sensitivity towards reactions with oxygen and hydrogen [1]. The reactivity with oxygen can be lowered by modifying the carbon surface in such a way that the number of sites, which are active in the oxidation, is lowered. These active sites (often referred to as the active surface area, ASA [2]) are responsible for the cyclic desorption of CO/CO_2 and adsorption of oxygen, which results in

burning the carbon support. The reactivity towards molecular hydrogen of bare activated carbon is low. Transition or noble metals, applied on this support, however, catalyze the hydro-gasification of carbon into methane. Two different mechanisms can be distinguished. The first type of hydro-gasification is metal catalyzed dissociation of hydrogen, which subsequently "spills over" to defects in the basal planes to form methane. Secondly, at temperatures higher than 100 K carbon can dissolve in the metal crystallite, diffuse to the gas-metal interface and react with hydrogen to methane. Research has primarily been focused on achieving an increased oxidation resistance by decreasing the ASA. A decrease in ASA can be achieved by heat treatment or impregnation with metal phosphates, chlorine compounds, and boron glasses [3,4], which all improve the oxidation resistance to a certain extent. Stegenga *et al.* [5] investigated the possibility of applying silicon carbide on the carbon surface. They impregnated activated carbon with tetraethoxysilane ($\text{Si}(\text{C}_2\text{H}_5\text{O})_4$, TEOS), which was subsequently decomposed into SiO_2 , followed by a heat treatment at 2273 K acquiring the SiC. This has resulted in an increase in oxidation resistance of 100 K, while a considerable amount of surface area was retained. Furthermore, the side crushing strength was improved by a factor two. An alternative method of modifying surfaces by SiC deposition to achieve an improvement in oxidation resistance is chemical vapour deposition (CVD). Thus, carbon/carbon composites are coated with silicon carbide which acts as a diffusion barrier for carbon and oxygen [6]. Another mode of operation exists in the surface modification and densification of porous substrates. This technique, referred to as chemical vapour infiltration (CVI), is one of the few in which ceramic composites can be manufactured consisting of undamaged fibres or whiskers embedded in a ceramic matrix. Thus, a very high toughness and strength can be combined, disclosing numerous applications of ceramic materials at demanding process conditions. Methyltrichlorosilane (CH_3SiCl_3 , MTS) is frequently used to achieve either an oxygen resistant SiC coating or a ceramic composite consisting of toughening fibres and a SiC matrix. Table 1 shows examples of this and several other SiC precursors and their application. To achieve an optimal oxidation resistance, it is important that stoichiometric SiC is deposited. Although the C/Si molar ratio in methyltrichlorosilane is one, deposition of silicon is encountered at temperatures below 1200 K, whereas carbon is co-deposited with SiC above 1800 K. The mechanism of SiC deposition can be regarded as two independent sub-systems, i.e. the deposition of carbon and the deposition of Si [22,23]. Equal rates will result in stoichiometric SiC. Detailed knowledge of the kinetics in the gas phase and on the surface is, however, limited, especially for chlorine containing SiC precursors like CH_3SiCl_3 . The gas-phase kinetics for the SiH_4 -hydrocarbon system is relatively well understood [19,20,24], here, more knowledge of the

surface chemistry is needed. Thermodynamic calculations are widely used for a first insight in the condensed phases which are stable under process conditions [22,23,25]. Furthermore, the gas-phase composition can be determined at thermodynamic equilibrium. Considering a certain amount of gaseous components (varying from 6 to 45), it has been shown that SiCl_4 and CH_4 are the most abundant Si and C components in the Si-Cl-C-H system below 1000 K. SiCl_2 and C_2H_2 are formed at temperatures higher than 1800 K. Deposition of stoichiometric SiC is predicted at certain $\text{H}_2/\text{CH}_3\text{SiCl}_3$ ratios which depend on temperature and pressure. On a thermodynamic basis, silicon co-deposition is found at high H/Si ratios, whereas carbon is co-deposited at low H/Si ratios.

In the present paper chemical vapour deposition of SiC is evaluated as a modification technique to achieve strong activated carbon particles with a high surface area and a high oxidation resistance. An obvious prerequisite, identifiable prior to this investigation, is the formation of SiC layers with the capability of shielding the underlying carbon substrate while retaining a major part of the porous structure. Thermodynamic calculations are carried out to establish preliminary indications for optimal deposition conditions by determining equilibrium gas-phase compositions and stable solid phases at various conditions. Reactive CVD (using the activated carbon as carbon source) and conventional CVD (using $\text{SiCl}_4/\text{CH}_4$ or CH_3SiCl_3) are performed on activated carbon extrudates and the thermodynamic calculations are evaluated. Subsequently, the oxygen reactivity, residual surface area, and side crushing strength are evaluated according to their modification technique. Finally, the infiltration process will be compared with the results obtained by mathematical modelling of CVI.

3. THERMODYNAMICS

Table 2 shows the gaseous and solid components which are incorporated in the calculations. The thermodynamic data (i.e. $\Delta_f H^{298 \text{ K}}$, $S^{298 \text{ K}}$, and $C_p^{800-2000 \text{ K}}$) are taken from JANAF Thermochemical Tables [26]. The calculations are carried out using atomic mass balances and minimization of the overall Gibbs energy using the programme Solgasmix [27]. It should be noted that only the relative amounts of atoms determine final thermodynamic equilibrium compositions, hence, no distinction can be made between carbon originating from graphite or methane. Thermodynamic calculations are carried out for atomic Si/(Si + C) ratios varying from 0 to 1 and for H/Si ratios of 40 and 400, at 10 kPa, and temperatures between 800 and 1800 K. Figure 1 displays an example of the mixture of gaseous components with equilibrium pressures exceeding 10^{-10} bar for the system Si/C = 1 and H/Si = 40. SiCl_4 and CH_4 are the most abundant gaseous SiC precursors at low temperatures. The equilibrium pressure of methyl-

Table 1. SiC precursors and their application

SiC precursor	Conditions of synthesis		Application	Ref.
	Temperature (K)	Pressure (kPa)		
CH ₃ SiCl ₃	1523–1873	n.r.	coating	[7]
	1400	1.7	coating	[8]
	1173–1273	10 to 35		[9]
	1173–1373	10 to 100	composite (CVI)	[10]
	1252–1270	2 to 13.3		[11]
CH ₃ SiCl ₃ /CH ₄	1473–1723	4.6	coating	[12]
SiCl ₄ /CH ₄	1400–1600	100	coating	[13]
(CH ₃) ₂ SiCl ₂	1473–1600	n.r.	coating	[14,15]
SiCl ₄ /Carbon	1500–1700	100	coating	[16–18]
SiH ₄ /C _x H _y	1773–1923	100	electronic	[19–21]

n.r. = not reported.

Table 2. Components used in thermodynamic calculations

Ar	HCl	CH ₄	CH ₂ Cl ₂	CCl ₃	SiHCl ₃	SiCl ₂
H	Si (s)	C ₂ H ₂	CH ₃ Cl	CCl ₄	SiH ₂ Cl ₂	SiCl ₃
H ₂	SiC (s, β)	C ₂ H ₄	C ₂ HCl	C ₂ Cl ₂	SiH ₃ Cl	SiCl ₄
Cl	C (s, graphite)	CHCl	CCl	C ₂ Cl ₄	SiH ₄	CH ₃ SiCl ₃
Cl ₂	CH ₃	CHCl ₃	CCl ₂	C ₂ Cl ₆	SiCl	—

Fig. 1. Equilibrium gas phase composition (including SiC, Si or carbon formation) for H₂/MTS = 20 and P = 10 kPa.

trichlorosilane does not exceed 10⁻⁸ bar, which originates from the low bonding energy of the Si–C bond (290 kJ/mol) in the MTS molecule relative to the Si–Cl (359 kJ/mol) and C–H bonds (338 kJ/mol). Above 1300 K the equilibrium pressure of SiCl₂ surpasses that of SiCl₄. The most abundant C-precursor shifts from methane to ethyne (C₂H₂) above 1700 K. The trends found in these calculations agree with those reported in the literature for the Si–H–Cl–C system. Figures 2 and 3 show the condensed phases in the temperature range of 800 to 1800 K as a function of the ratio of silicon and carbon in the

system. The effect of H/Si ratio has been investigated as well.

Three areas are encountered in Fig. 2, i.e. regions of SiC + C, SiC, and SiC + Si deposition. Increasing the H/Si ratio from 40 (Fig. 2(a)) to 400 (Fig. 2(b)) results in a broader range of conditions in which Si is co-deposited, silicon is exclusively present at high Si/C ratios and low temperatures. This evolves from the equilibrium shift of the following reaction to the right-hand side:

Furthermore, the region in which solid carbon is present decreases in size with increasing amounts of hydrogen at temperatures below 1200 K. This is the consequence of the equilibrium shift of the following reaction to the right-hand side:

The CVD diagrams have also been determined at 100 kPa (1 bar). Qualitatively, no differences are found compared to Fig. 2, except for the low temperature SiC area. This region is somewhat extended into the SiC + C region.

From these calculations it can be generally concluded that equimolar amounts of Si and C in the system are beneficial for stoichiometric SiC deposition. Furthermore, increasing the H/Si ratio from 40 to 400 decreases the amount of solid carbon, whereas the amount of co-deposited Si is increased. This might suggest optimal conditions for SiC deposition at H₂/SiCl₄ ratios below 40. The reverse of reaction SiCl₄ + 2H₂ + C ⇌ 4HCl + SiC, however, becomes significant at very low H₂/HCl ratios and thus a minimal excess of hydrogen is indispensable for SiC formation.

Fig. 2. (a) CVD diagram for $\text{H}_2/\text{SiCl}_4 = 20$ and $P = 10$ kPa. Condensed phases as a function of gas-phase composition and temperature. (b) CVD diagram for $\text{H}_2/\text{SiCl}_4 = 200$ and $P = 10$ kPa. Condensed phases as a function of gas-phase composition and temperature.

Fig. 3. Pore volume distribution of RW08.

4. EXPERIMENTAL

4.1 Materials

The modifications have been performed on steam activated, peat based, Norit activated carbon extru-

dates, type RW08. Prior to modification, the extrudates were separated according to degree of activation. The properties of the fraction used are shown in Table 3. The pore size distribution for the meso- and macro-pore region, determined by mercury porosimetry [28], is shown in Fig. 3. The typical poly-disperse porous structure [29] is evident. Two major contributions to the macro-pore structure are displayed, pores with radii of 250 and 1000 nm. The micro-pore region cannot be identified with Hg-porosimetry.

Hydrogen (99.99%), Ar (99.99%), and CH_4 (99.995%) were obtained from Hoek Loos. Purification of the gases was carried out by passing them through a bed of $\text{Pd}/\text{Al}_2\text{O}_3$ (hydrogen) or $\text{Cu}/\text{Al}_2\text{O}_3$ (Ar, CH_4) followed by a molecular sieve (5A) for water removal. Silicon tetrachloride (99%) was obtained from Aldrich Chemical Company, methyltrichlorosilane (98%) from Janssen Chimica, and were all used without further purification. Graphite plates ($10 \times 5 \times 1$ mm) were obtained from Johnson Matthey (batch 35142).

4.2 Chemical vapour deposition of silicon carbide

A schematic diagram of the CVD apparatus is shown in Fig. 4. A thin bed of extrudates (200 mg, 1 mm bed length) was positioned in a hot-wall tubular quartz reactor (internal diameter of 42 mm) to assure deposition under differential conditions. Prior to CVD, the substrates were heated in hydrogen with 0.167 K/s up to 1400 K (above the highest deposition temperature applied), followed by cooling to the deposition temperature, and adjusting to sub-atmospheric pressure. A graphite substrate, which was placed just upstream of the extrudates, was used to determine the rate of SiC deposition. The reactant gas was composed by bubbling argon through an evaporator filled with SiCl_4 or MTS (held at 410 or 400 K, respectively), which was subsequently mixed with hydrogen (and CH_4) before entering the reactor. The total gas flow rate equalled 5.6 ml/s (STP) and 27.8 ml/s (STP) for the SiCl_4 and CH_3SiCl_3 experiments, respectively.

4.3 Scanning electron microscopy

The activated carbon extrudates and graphite substrate were analyzed by scanning electron microscopy (JEOL JSM-35, Au sputtering of 4 minutes) to investigate the morphology of the deposited material. Furthermore, the growth rate has been determined from the layer thickness on the graphite substrate. From a representative area, a micrograph was taken and a mean thickness was determined by measuring the SiC layer at 11 places at equal distance from each other [30].

4.4 Surface area measurements

Nitrogen isotherms at 77 K were recorded on a Carlo Erba Sorptomatic 1800. Prior to measurement the samples were degassed at 423 K and 0.1 kPa. The BET surface area (S_{BET}), t surface area (S_t) and micro-

Table 3. Physical properties of the activated carbon extrudates

S_{BET} (m^2/g)	V_{pore} (ml/g)	S_1 (m^2/g)	V_{micro} (ml/g)	$\rho(\text{Hg})$ (kg/m^3)	$\rho(\text{He})$ (kg/m^3)	Ash (wt%)	Length (mm)	Diameter (mm)
947	0.60	112	0.41	661	2167	5.2	3.0	0.81

Fig. 4. Scheme of the CVD apparatus.

pore volume (V_{micro}) were determined according to the literature [31,32].

4.5 Temperature programmed desorption

Temperature programmed desorption (TPD) is carried out on home-made equipment by heating 200 mg activated carbon with 0.167 K/s to 1273 K in a helium–argon gas mixture (97/3 v/v). The gases evolved were recorded by a mass spectrometer (Varian Mat44 S) in multiple ion detection mode. Calibration was carried out by decomposing calcium oxalate monohydrate.

4.6 X-ray diffraction

Diffraction patterns were recorded on home-made equipment using a $\text{Cu-K}\alpha$ beam by measuring the Debye–Scherrer pattern.

4.7 Thermogravimetric analysis

A Setaram TAG 24 S thermobalance was used to determine the oxidation resistance. The samples (~ 30 mg) were heated with a heating rate of 0.167 K/s in air to 1273 K, while recording the weight change. The temperature at the point of maximum rate of weight loss (T_{max}) is generally assumed to be a suitable property for comparing the oxidation resistance of the activated carbon.

4.8 Side crushing strength

The side crushing strength was determined with a Schleuniger-2E. The average value of ten samples was used.

5. RESULTS

5.1 Pretreatment

Heating the activated carbon in hydrogen up to 1400 K (this first step of the modification procedure

will be referred to as the pretreatment), resulted in a total weight decrease of 8.4%. The difference in oxidation behaviour compared to the original carbon is depicted in Fig. 5. The hydrogen pretreatment increases the resistance against oxidation by 80 K. This is shown by the identical increase in temperature at which the oxidation starts and the temperature at the maximum rate of oxidation (T_{max}). The improvement in oxidation resistance is the result of reducing the ASA by decomposing the oxygen containing surface groups into H_2O , CO_2 , and CO , and no significant change in TSA. Thus, the number of defects in the graphitic structure and, hence the oxygen reactivity, has been decreased. The decomposition of the oxygen containing surface groups of the fresh carbon during this initial step has been analyzed by temperature programmed desorption in a helium–argon mixture. The results are shown in Fig. 6. Single oxygen functional groups generally produce CO onto decomposition of carbon–oxygen complexes, whereas CO_2 is formed from decomposing carboxylic acids. The weight losses of H_2O , CO_2 , and CO were 2.4, 3.0, and 1.7 wt%, respectively. The total weight loss is somewhat lower than that during the H_2 pretreatment. SEM analysis of the extrudates prior and after the pretreatment showed that the macro-structure does not change. Figure 7(a) and (b) are indicative for the structure of the carbon extrudates after the H_2 pretreatment. Conglomerated

Fig. 5. Carbon conversion (ζ) and the first derivative ($d\zeta/dT$) for the original (—) and H_2 -pretreated (---) carbon during TGA in air (heating rate 0.167 K/s).

Fig. 6. Temperature programmed desorption of H_2O , CO_2 , and CO from fresh RW08.

carbon particles of a grained structure can be distinguished, which are typical for a steam activated carbon. The outer surface appears to consist of granules of smaller diameter, as displayed in Fig. 7(b). The side crushing strength of the original and pretreated carbon was identical, i.e. 20.9 ± 4.7 N.

In the following section, the three types of SiC formation will be discussed separately. The activated carbon which has been heated to 1400 K in H_2 will be taken as reference material in all cases.

5.2 Reactive CVD of SiCl_4 on activated carbon ($\text{C} + \text{SiCl}_4 + 2\text{H}_2 \rightarrow \text{SiC} + 4\text{HCl}$)

A ratio of H_2/SiCl_4 equal to 20 has been used in all cases. The CVD temperature ranged from 880 to 1380 K. After modification no differences in colour are encountered. Figure 8 displays the amount of solid deposits, determined by TGA, and T_{max} as a function of deposition temperature. It is shown that the deposited amount decreases with increasing temperature and that the oxidation resistance has only slightly been improved compared to the H_2 pretreated carbon. XRD revealed only silicon as crystalline phase, no crystalline SiC has been detected.

5.3 CVD of SiC using SiCl_4 and CH_4 on carbon ($\text{SiCl}_4 + \text{CH}_4 \rightarrow \text{SiC} + 4\text{HCl}$)

The results of this modification are displayed in Table 4. The use of methane as an additional carbon source results in sole SiC deposition at a reaction temperature of 1375 K. Silicon deposition is encountered at lower temperatures. Activation of relatively stable methane is probably the rate limiting step in the formation of SiC. An additional improvement (compared to the H_2 pretreated carbon) in oxidation resistance of 75 K has been achieved after reaction at 1375 K. The side crushing strength of this sample was 35.9 ± 5.6 N, which is an improvement of a factor 1.7 compared to the original carbon.

It should be noted although the activated carbon contains large amounts of ash components, which can act as gasification agent (see Table 3), an experiment of only SiCl_4 and H_2 in the vapour phase did not result in the formation of any SiC.

(a)

(b)

Fig. 7. Morphology of (a) the external surface and (b) the internal surface of RW08 after H_2 treatment.

5.4 CVD of SiC using CH_3SiCl_3 on activated carbon ($\text{CH}_3\text{SiCl}_3 \rightarrow \text{SiC} + 3\text{HCl}$)

After modification with methyltrichlorosilane above 1220 K, the extrudates and graphite substrate were covered with a shiny metallic grey film. X-ray diffraction showed deposition of stoichiometric β -SiC. SEM analysis revealed a cauliflower-like SiC morphology, as shown in Fig. 9(a) and (b), which is the typical SiC structure resulting from using this precursor.

Fig. 8. Deposited amount (+) and $T_{\max}$ (Δ) as a function of deposition temperature.

Table 4. Modification of activated carbon by CVD using $\text{H}_2/\text{SiCl}_4/\text{CH}_4$ (reaction time = 6 hours)

H_2/SiCl_4 (mol/mol)	$\text{CH}_4/\text{SiCl}_4$ (mol/mol)	T (K)	P (kPa)	Deposited amount (g/g _{carbon})	$T_{\max}$ (K)	S_{BET} (m ² /g)	V_{pore} (ml/g)
170	1.8	1091	10	0.28 (Si)	945	431	0.23
170	1.8	1376	10	0.30 (SiC)	1025	176	0.12

sor under these conditions [33]. Deposition of SiC on graphite results in a more compact and dense layer than on activated carbon, which originates from the less rougher surface morphology. A crack in the SiC layer sometimes appears after prolonged deposition, which is caused by differences in expansion coefficients between graphite/activated carbon and SiC. Differences in nucleation can easily be identified from Fig. 9(b) and (c). The number of nucleation sites on activated carbon exceeds that of graphite as shown by the initially more grained structure of the first SiC deposited on activated carbon. The first phase of growth in a CVD process results in a thin microcrystalline layer of random orientation, imposed by the roughness of the substrate surface and barely limited growth of the first nuclei [34]. The influence of the substrate surface decreases at increasing layer thicknesses; a finely denticulated morphology is then formed, on top of which multi-star twin tips can be discerned. Owing to the extensive surface roughness of activated carbon, this grained SiC morphology remains visible even at substantial SiC layer thicknesses. Figure 9(d) displays a top-view of SiC deposited on activated carbon. As can be seen in this micrograph the major part of the deposited SiC is present within the outershell of the extrudates up to 100 μm . The porous structure is still evident, while cracks probably originate from the different expansion coefficient between the SiC and the activated carbon, as can be seen in Fig. 9(c). This difference will cause the SiC layer cracks during cooling from deposition temperature to room temperature.

5.4.1 Oxygen reactivity The $T_{\max}$ of the modified extrudates varies between 985 and 1120 K, sug-

gesting an additional increase in oxidation resistance of 35 to 170 K. The establishment of the exact position of the $T_{\max}$ is, however, difficult, owing to various maxima in the first derivative as displayed by Fig. 10. Four maxima in the range of about 950 to 1150 K can be distinguished for a heating rate of 0.167 K/s. The number of maxima decreases with decreasing heating rates (0.0167 and 0.00833 K/s), pointing to the limitation of oxygen diffusion into the extrudate during oxidation by inhomogeneous carbon overlayer protection than the existence of different SiC species, which results in different onsets of oxidation.

5.4.2 Textural properties Textural properties are of primary importance for utilizing these modified activated carbon extrudates as catalyst support. Table 5 displays the surface area and pore volume for several extrudates. For convenience, the data are also presented normalized to initial amount of carbon. This allows additionally the identification of the amount of surface area and pore volume lost solely by the weight increase due to SiC deposition. The surface areas (total and micro) and pore volumes (total and micro) after modification declined by around 50% of the initial value. Half of this decrease can be attributed to the weight increase due to SiC deposition. The remainder is probably caused by blocking parts of the porous structure.

5.4.3 Side crushing strength Analysis of the strength of the modified activated carbon results in the 95% confidence regions of the side crushing strength (SCS) as displayed in Fig. 11. The extrudates are strengthened by an average factor of 1.4 after SiC-CVD modification. A direct relationship between

Fig. 9. (a) Surface of SiC deposited on a graphite plate. (b) Side view of SiC deposited on a graphite plate. (c) Side view of SiC deposited on activated carbon. (d) Surface of SiC deposited on activated carbon.

the synthesis procedures and corresponding SCS is, however, difficult to obtain.

5.4.4 Kinetics of SiC deposition The reaction rate of SiC formation has been determined by measuring the layer thickness of SiC deposited on the graphite substrates. The growth rate at 1222 and 1273 K as a function of the MTS concentration is shown in Fig. 12. Figure 13 displays the corresponding Arrhenius plot. The dependence of reaction rate

on the concentration appears to be negligible in the parameter range investigated. A zero order dependence of the concentration on the reaction rate can be assumed based on Figs 12 and 13.

6. DISCUSSION

6.1 Evaluation of the catalyst support properties

In the modification of activated carbon by SiC-CVD a compromise has to be met. First, the SiC

Fig. 10. Conversion and first derivative of a MTS modified carbon during TGA in air, heating rate: 0.00833 K/s (—), 0.0167 K/s (---), and 0.167 K/s (····).

Fig. 12. Rate of SiC formation as a function of MTS concentration at 1223 K (○) and 1273 K (Δ). The lines are used to guide the eye.

Table 5. Textural properties of SiC-CVD modified activated carbon

Conditions		Textural properties							
$T(K)$	C_{MTS} (mmol/m ³)	S_{BET} (m ² /g, m ² /g _c)	V_{pore} (ml/g, ml/g _c)	S_t (m ² /g, m ² /g _c)	V_{micro} (ml/g, ml/g _c)				
1273 (2)	100	532	729	0.33	0.46	49	67	0.23	0.32
1242 (3)	102	533	712	0.33	0.44	53	71	0.23	0.31
1222 (4)	104	512	672	0.31	0.41	44	58	0.23	0.30
1223 (5)	42.6	576	712	0.37	0.45	60	74	0.25	0.31
1224 (6)	140	510	712	0.31	0.43	45	63	0.23	0.32
1223 (7)	69.8	571	714	0.35	0.43	47	59	0.26	0.33
1273 (8)	134	471	670	0.28	0.40	38	54	0.21	0.30

The numbers in brackets refer to Fig. 16 and Table 7.

Fig. 11. Confidence regions (95%) of the side crushing strength (SCS) for various modified carbons. The experiment numbers refer to Table 5.

layer has to be thick and dense, and uniformly deposited in the pores to ensure a considerable strength improvement, and to guarantee adequate protection against oxidation. Secondly, a sufficiently large surface area has to be available after modification for catalyst support applications. This means

Fig. 13. Arrhenius plot for various MTS concentrations: 4.33 mol% (+); 10.5 mol% (Δ); and 14.2 mol% (○). The lines are used to guide the eye.

that the SiC layer has to be as thin as possible. This controversy should be borne in mind when evaluating the various properties of the modified activated carbon. Reactive CVD is on first sight an elegant way to achieve both objectives. Here, the activated carbon acts as the carbon source for SiC formation. Hence, deposition of SiC is expected to be limited to the surface where carbon is exposed to SiCl_4 . Utilization of an additional gaseous carbon source (e.g. CH_4 , CH_3SiCl_3) can enhance the deposition rate. A selective deposition, however, cannot be obtained. In the section below, the influence of the pretreatment and modification technique on the oxidation resistance and mechanical strength will be discussed in detail. Heating activated carbon extrudates to the temperature for SiC deposition results in changes in the surface composition of the substrates. Comparison of the pretreatment in hydrogen and an argon-helium mixture results in comparable amounts of desorbed molecules, i.e. 8.5 and 7.1 wt%, respectively. The difference can be explained by the difference in final temperature, i.e. 1400 and 1273 K, respectively. The presence of hydrogen is expected to alleviate the decomposition of the oxygen containing surface groups (e.g. by termination of the dangling bonds which remain on the surface after decomposition). However, the total amount of desorbed molecules at temperatures above the synthesis temperature of the activated carbon (around 1300 K) is expected to be roughly similar in argon and hydrogen regarding the inertness of graphite in hydrogen environments. Two conclusions can be drawn from these observations. First, the amount of oxygen containing surface groups on activated carbon decreases significantly during heating to the temperature of deposition. This will substantially decrease the ASA and, hence, the oxygen reactivity. The T_{max} is elevated by 80 K compared with the untreated carbon. Additionally, since the formation of SiC is expected to start at surface defects (i.e. oxygen containing functional groups) in the graphite lattice, the number of nucleation sites for SiC growth will diminish as well. This might result in differences in the morphology of the SiC layer, and thus the oxidation resistance. Secondly, desorption of CO starts at a temperature of 1050 K and just drops off after an isothermal period of one hour at 1273 K, which implies that the ASA is changing in the major part of the pretreatment trajectory. To achieve an identical starting material in all experiments, similar pretreatments are indispensable to assure the presence of identical amounts of oxygen containing functional groups and, hence, an identical oxygen reactivity and similar amounts of nucleation sites for SiC formation at the start of the experiment. These considerations have been the basis for utilizing the pretreatment procedure as described above.

Typical TGA profiles of all types of modification are displayed in Fig. 14. It is evident that, except for the MTS modification, T_{max} represents a good parameter for the evaluation of the oxidation resistance.

Fig. 14. Carbon conversion and first derivative of various modifications during TGA in air, heating rate 0.167 K/s: (a) RH08, (b) H_2 -pretreated, (c) SiCl_4 , (d) $\text{CH}_4/\text{SiCl}_4$, and (e) CH_3SiCl_3 .

Oxidation of the MTS modified carbons results in an increased T_{max} , although the start of the oxidation is similar to that of the original carbon. This means that no real improvement in oxidation resistance has been achieved and that the increment in T_{max} originates from diffusion limitations of oxygen during oxidation.

6.1.1 Reactive CVD using SiCl_4 RCVD at temperatures below 1400 K shows no significant increase in T_{max} . In all cases considerable amounts of silicon are deposited which proves that RCVD is not a suitable technique for attaining improvements in the oxidation resistance. Thermodynamically, silicon carbide deposition is found to be possible at temperatures above 800 K. Hence, it is concluded that SiC formation is kinetically controlled by the low reactivity of the activated carbon, resulting in silicon deposition.

6.1.2 CVD of SiC using a mixture of SiCl_4 and CH_4 From the results presented above, it can be concluded that both objectives (improvement of oxidation resistance and mechanical strength) can simultaneously be achieved by SiC-CVD using a $\text{CH}_4/\text{SiCl}_4$ mixture at 1380 K. The oxidation resistance increases by 150 K (80 K for the pretreatment and 70 K by SiC deposition) with a concomitant side crushing strength improvement of a factor 1.7. The surface area of this material equals 176 m^2/g , which suffices for catalytic purposes. The decrease in S_{BET} originates mainly from blocking the micro-pore structure which implies that infiltration of SiC has been achieved. The results support the conclusion that this type of SiC deposition indeed lowers the oxygen

reactivity and that the low reactivity of the activated carbon limits the SiC formation in the RCVD set-up.

6.1.3 CVD of SiC using CH_3SiCl_3 Deposition of stoichiometric β -SiC has been achieved at 1200 K utilizing MTS as precursor. The oxidation resistance is, however, *reduced* compared to the H_2 -treated carbon. Curve e in Fig. 14 displays the early onset of oxidation, which might originate from the presence of hydrogen chloride (HCl) during deposition, which can restore a part of the ASA lost during the H_2 pretreatment. The side crushing strength improved by a factor 1.4. The deposition of SiC at the exterior of the particle has imposed diffusion problems for oxygen during oxidation, which resulted in multiple T_{max} values for one sample. The presence of this layer will undoubtedly aggravate the mass transfer towards the particle, and thus limit the use as catalyst support at high temperatures.

6.2 Evaluation of the MTS-CVI technique

MTS is a well known SiC precursor for the synthesis of SiC based composites, which allows evaluation of the modification in comparison with those reported in the literature. No influence of MTS concentration on the reaction rate could be distinguished. It should, however, be noted that the number of these experiments is not sufficient by far to determine the crucial parameters of SiC deposition from MTS. However, qualitative trends can be determined. The reaction order with respect to MTS appears to be zero order, which is in accordance with the results obtained by Loumagne *et al.* [35]. The activation energy calculated from the Arrhenius plot amounts to 279 ± 17 kJ/mol with a pre-exponential factor of $7.26 \pm 0.64 \times 10^7 \text{ mol m}^{-2} \text{ s}^{-1}$. This activation energy is considerably higher than that reported by Loumagne *et al.*, i.e. 160 kJ/mol. To explain this discrepancy, it is illustrative to display several kinetic expressions which have appeared in the literature during the last decade (Table 6). The difficulty in kinetic modelling lies in the fact that SiC formation from MTS is governed by gas-phase decomposition reactions as well as by surface reactions. This means that the reactor geometry (e.g. the volume surface area ratio) and other experimental parameters like residence time of MTS in the hot zone of the reactor will influence the activation of MTS significantly. Gas-phase decomposition has been analyzed theoretically

[39] and experimentally by mass spectrometry [40]. SiCl_4 , HCl, and CH_4 species are observed on decomposing MTS in hydrogen at 1428 K and 100 kPa. These results agree fairly well with the equilibrium pressures shown in Fig. 1. However, the way to extract information from these data establishing the active species in the SiC formation is ambiguous. It might be anticipated that MTS and a $\text{SiCl}_4/\text{CH}_4$ mixture show identical deposition characteristics. However, the SiC reaction rate and morphology from a $\text{SiCl}_4/\text{H}_2/\text{CH}_4$ and MTS/ H_2 mixture differ significantly. Furthermore, compared to a $\text{SiCl}_4/\text{CH}_4$ mixture, the temperature necessary to deposit crystalline SiC is 200 K lower using MTS. This probably results from the gas-phase formation of CH_3 radicals from MTS, which increases the reactivity of the carbon precursor:

Thus, stoichiometric SiC can be deposited at lower temperatures compared with the $\text{SiCl}_4/\text{H}_2/\text{CH}_4$ mixture. From this it is evident that the rate of decomposition of MTS and reaction or recombination of radicals will have a major influence on the kinetics found for SiC deposition. This aspect of MTS as SiC precursor is one of the origins of disagreements between the kinetic models found by various authors, using different reactor set-ups.

The exact amount of SiC which is deposited inside the extrudates has to be estimated in order to assess the infiltration performance of the SiC-CVI procedure. The rate expression of SiC deposition based on the data given above is:

$$R = 7.26 \times 10^7 \exp \left[\frac{-279000}{RT} \right] \quad (4)$$

Typical reaction rates are 1–4 nm/s at 1223 and 1286 K, respectively. The polydisperse porous structure of activated carbon hampers the determination of a mean pore radius and, hence, (1) the pore closure time, (2) the amount of SiC deposited inside and outside the pores, and (3) the effective diffusion coefficient of methyltrichlorosilane. As a first rough estimate, the largest pores ($r = 1000$ nm, $V_{\text{pore}} = 0.6 \text{ cm}^3/\text{g}$) are assumed to determine the infiltration process. The smaller pores are supposed to be closed in the early stage of the infiltration process. The time necessary for pore closure of the 1000 nm pores is determined using eqn (4). SiC is deposited at the exterior of the extrudate in the remaining process period. The amount of SiC deposited after pore closure is subtracted from the total amount of deposited SiC. This yields the amount of SiC infiltrated in the porous structure. Subsequently, the residual porosity is calculated. The results are displayed in Table 7. The amount of deposited SiC varies between 0.22 and 0.42 $\text{g}_{\text{SiC}}/\text{g}_{\text{carbon}}$. No correlation is found between the reaction rate and total amount of SiC deposited on the carbon. The infiltration (SiC infiltration) ranges from 21 to 94% and improves for (a) decreasing temperatures and (b) increasing concentrations of MTS. The first effect is commonly

Table 6. Reported kinetic models for SiC deposition from MTS

Experimental conditions			$k_0 \exp(-E_a/RT) C_{\text{MTS}}^n$		
T (K)	P (kPa)	H_2/MTS	n	E_0 (kJ/mol)	Ref.
1073–1373	100	0.5–1	1	120	[36]
1250–1300	3.3	5–20	0	188	[37]
1073–1373	20	0.7–4	1	255	[38]
1175–1225	5–10	1–5	0.1–1	160 ± 40	[35]
1075–1125	5–10	3–5	2.5	>300	[35]

Table 7. Infiltration of SiC in activated carbon

Exp. no.	Experimental conditions			Deposition characteristics		
	<i>T</i> (K)	<i>C</i> _{MTS} (mmol m ⁻³)	<i>P</i> (kPa)	<i>R</i> × 10 ⁵ (mol m ⁻² s ⁻¹) ^a	Depos. amount (m _{SiC} /m _{carbon})	SiC infiltr. (%)
1	1286	40.5	10	36.5	0.224	21.3
2	1273	100	10	27.2	0.371	66.3
3	1242	102	10	15.8	0.336	81.3
4	1222	104	10	10.4	0.313	89.4
5	1223	42.6	10	9.2	0.236	88.7
6	1224	140	10	8.56	0.397	94.2
7	1223	69.8	5	7.33	0.250	93.4
8	1273	134	10	27.9	0.423	69.5

^a Determined from SiC deposition on graphite.

encountered in CVI-processes; by reducing the reaction rate with respect to the diffusion rate, infiltration is enhanced, resulting in higher amounts of SiC in the pores. The second effect originates from the zero-order rate expression found for MTS. Increasing the MTS concentration does not affect the deposition rate of SiC. However, an increase in bulk concentration of MTS imposes a higher concentration gradient in the pore (and hence a higher diffusion rate). Moreover, depletion of MTS will occur at higher infiltration depths compared to lower bulk MTS concentrations.

To compare the influence of deposition conditions on the residual porosity, a plot of the residual porosity versus the Thiele modulus is applied. The Thiele modulus for a *n*th order reaction is derived similarly to the procedure described elsewhere [41]. The tortuosity is assumed to be 4 [42]. The gas-phase diffusion coefficient is taken from Sheldon and Besmann [11]. The total void fraction of the extrudates is derived from the He and Hg densities given in Table 3, and equals 0.666. This results in an initial void fraction for pores with radii larger than 1000 nm (*V*_{pore, *r* > 1000 nm} = 0.6 ml/g, Fig. 4) of 0.40. The calculation of the surface area of this pore system is based on the pore volume of the region of the 1000 nm pores, i.e. 0.2 ml/g (Fig. 4), and equals 0.4 m²/g. From these numbers the effective diffusion coefficients and the corresponding Thiele moduli are determined. For a full evaluation the Thiele moduli are to be related to the residual porosity of the extrudates. The residual porosity is defined in the following equation:

$$\epsilon = \frac{\left(V_{\text{pore, } r > 1000\text{nm}} \right)_{\text{final}}}{\left(V_{\text{pore, } r > 1000\text{nm}} \right)_{\text{initial}}} \quad (5)$$

The results of the calculations are shown in Table 8.

A similar approach had previously been applied to

Table 8. Thiele moduli and residual porosities for the MTS modified activated carbons

Exp. no.	1	2	3	4	5	6	7	8
ϕ	2.47	1.38	0.99	0.79	1.25	0.70	0.96	1.19
ϵ	0.97	0.87	0.85	0.85	0.89	0.80	0.88	0.84

the results of the mathematical modelling of isothermal chemical vapour infiltration [41]. The CVI process had been modelled as a transient process in which the pore geometry changes in time owing to the deposition of solids. The influence of various types of surface kinetics on the deposition profile and the porosity of the material after pore closure had been evaluated. A general correlation had thus been found between the residual porosity and the Thiele modulus, which was independent of the kinetic model implemented. This correlation or design chart is fitted by eqn (6) which is based on the equation that describes the relationship between the effectiveness factor and Thiele modulus in heterogeneous catalysis.

$$\epsilon = 1 - \frac{3}{a - \phi} \left[\frac{1}{\tanh(a - \phi)} - \frac{1}{a - \phi} \right] \quad (6)$$

where the constant *a* equals 20 ± 1 (95% confidence region) which shows that more stringent values of the Thiele modulus are needed to arrive at low residual porosities compared to reaching an effectiveness factor of one in the initial stage of the densification process. Figure 15 displays the Thiele moduli and corresponding residual porosities of the experiments reported in Table 7 relative to the design chart. For comparison, data reported by Sheldon and Besmann [11] are included. Their results are obtained from the infiltration of a carbon fibre bundle with SiC. The average pore diameter of this preform

Fig. 15. The residual porosity (ϵ) versus the Thiele modulus (ϕ) for data of Table 7 (+) and from Ref. [11] (Δ). The solid lines embody the 95% confidence region of the design chart [41].

ranges typically from 10 to 20 μm , which explains the considerably lower residual porosities achieved by these authors compared to those obtained for the modification of the activated carbon extrudates.

The theoretical design chart and experimentally obtained data display a good correlation for infiltrations in both low and high residual porosity regimes. This allows the use of Fig. 15 as a convenient pre-experimental design chart for optimization of CVI procedures. Numerical modelling and experimental validation are, of course, still indispensable for evaluating the process and the material produced.

7. CONCLUSION

Modification of activated carbon by SiC-CVD using $\text{SiCl}_4/\text{CH}_4$ results in improvements in oxidation resistance (up to 170 K) as well as in the side crushing strength (factor 1.7). The residual surface area is 176 m^2/g , which suffices for catalyst support applications. Additional advances require properties of the SiC layer to be deposited on the carbon surface which are conflicting to the characteristics necessary for catalyst support utilization, i.e. a thin SiC coating to ensure the preservation of sufficient surface area. Selective deposition by reactive CVD cannot be achieved below 1400 K, silicon deposition has been encountered in all situations. Application of CH_3SiCl_3 (MTS) embodies the use of an additional gaseous carbon source. Here, SiC deposition and infiltration have been observed. The oxidation resistance did not improve; the side crushing strength enhanced by a factor of 1.4. Utilization of these modified extrudates as catalyst support is feasible regarding their final specific surface area of 530 m^2/g . A zero-order relationship was found between the MTS concentration and the rate of SiC formation, the activation energy has been found to be 279 kJ/mol. The quantity of SiC deposited inside the extrudates ranges from 20 to 95% of the total amount deposited. Comparison of the residual porosity of the extrudates with an earlier mathematically developed chemical vapour infiltration design chart shows good agreement. [7–10, 12–18, 21, 36–38]

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REFERENCES

1. H. Jüntgen, *Fuel* **65**, 1436 (1986).
2. N. R. Laine, F. J. Vastola and P. L. Walker, *J. Phys. Chem.* **67**, 2030 (1963).
3. N. Murdie, E. J. Hippo and W. Kowbel, In *Proc. Carbon '88, Internat. Carbon Conf.*, p. 74 (1988).
4. P. Vast, G. Palavit, L. Montagne, J. L. Boulliez and J. Cordier, In *Proc. Carbon '88, Internat. Carbon Conf.*, p. 582 (1988).
5. S. Stegenga, M. van Waveren, F. Kapteijn and J. A. Moulijn, *Carbon* **30**, 577 (1992).
6. D. B. Stinton, T. M. Besmann and R. Lowden, *Ceram. Bull.* **67**, 350 (1988).
7. D. J. Cheng, W. J. Shyy, D. H. Kuo and M. H. Hon, *J. Electrochem. Soc.* **134**, 3145 (1987).
8. F. J. Buchanan and J. A. Little, *Surf. Coat. Technol.* **46**, 217 (1991).
9. E. Fitzer, W. Remmele and G. Schoch, In *Proc 7th European Conf. on CVD*, Journal de Physique, C5-209 (1989).
10. F. Christin, R. Naislain and C. Bernard, In *Proc 7th Int. Conf. on CVD* (edited by T. O. Sedwick and H. Lydtin), p. 499. Electrochemical Society, Princeton, (1979).
11. B. W. Sheldon and T. M. Besmann, *J. Am. Ceram. Soc.* **74**, 3046 (1991).
12. D. H. Kuo, D. J. Cheng and W. J. Shyy, *J. Electrochem. Soc.* **137**, 3688 (1990).
13. A. Parretta, A. Camanzi, G. Giunta and A. Mazzarano, *J. Mater. Sci.* **26**, 6057 (1991).
14. T. Kaneko, T. Okuno and H. Yumoto, *J. Crystal Growth* **91**, 599 (1988).
15. T. Kaneko, T. Okuno and I. Kabe, *J. Crystal Growth* **108**, 335 (1991).
16. H. Vincent, J. L. Ponthenier, L. Porte, C. Vincent and J. Bouix, *J. Less Comm. Met.* **157**, 1 (1990).
17. H. Vincent, J. L. Ponthenier, C. Vincent and J. Bouix, *Rev. Sci. Technol. Def.* **2**, 89 (1988).
18. J. Bouix, M. Cromer, J. Dazord, H. Mouricoux, J. L. Ponthenier, J. P. Scharff, C. Vincent and H. Vincent, *Rev. Int. Hautes Tempér. Refract. Fr.* **24**, 5 (1987).
19. C. D. Stinespring and J. C. Wormhoudt, *J. Crystal Growth* **87**, 481 (1988).
20. J. H. Koh and S. I. Woo, *J. Electrochem. Soc.* **137**, 2215 (1990).
21. J. M. Harris, H. C. Gatos and A. F. Witt, *J. Electrochem. Soc.* **118**, 335 (1971).
22. J. E. Doherty, *J. Metals* **6**, 6 (1976).
23. G. S. Fischman and W. T. Petuskey, *J. Am. Ceram. Soc.* **68**, 185 (1985).
24. M. D. Allendorf and R. J. Kee, *J. Electrochem. Soc.* **138**, 841 (1991).
25. A. I. Kingon, L. J. Lutz, P. Liaw and R. F. Davis, *J. Am. Ceram. Soc.* **66**, 558 (1983).
26. M. W. Chase Jr, C. A. Davies, J. R. Downey Jr, D. J. Frurip, R. A. McDonald and A. N. Syverud, JANAF Thermochemical Tables, *J. Phys. Chem. Ref. Data* **14** (1985).
27. G. Erikson, *Chemica Scripta* **8**, 100 (1975).
28. Internal report A8804, Norit Research Laboratory (1991).
29. H. Jankowska, A. Swiatkowski and J. Choma, *Active Carbon*, p. 79. Ellis Horwood, New York (1991).
30. *Perry's Chemical Engineers' Handbook*, 6th edn, pp. 2–85. McGraw-Hill, New York (1984).
31. S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).
32. J. H. de Boer, B. G. Linsen and Th. J. Osinga, *J. Catal.* **4**, 643 (1965).
33. F. J. Buchanan and J. A. Little, *Surf. Coat. Technol.* **46**, 217 (1991).
34. D. J. Cheng, W. J. Shyy, D. H. Kuo and M. H. Hon, *J. Electrochem. Soc.* **134**, 3145 (1987).
35. F. Loumagne, F. Langlais and R. Naslain, in *Proc. 9th European Conf. on CVD*, (edited by T. Mäntylä), p. 527 (1993).
36. K. Brennfleck, E. Fitzer, G. Schoch and M. Dietrich, In *9th Int. Conf. on CVD* (edited by M. D. Robinson *et al.*), p. 649. Electrochemical Society, Pennington, NJ (1984).
37. T. M. Besmann and M. L. Johnson, In *Proc. Int. Symp. on Ceramic Materials and Components for Engines* (edited by V. J. Tennery). American Ceramic Society, Westerville, OH (1989).
38. E. Fitzer, W. Fritz and G. Schoch, *High Temp. High Pres.* **24**, 343 (1992).
39. M. D. Allendorf, C. F. Melius and T. H. Osterheld, In *12th Int. Conf. on CVD*, PV 93-2 (edited by K. F. Jensen and G. W. Cullen), p. 20. Electrochemical Society, Pennington, NJ (1993).
40. Y. Yeheskel, S. Agam and M. S. Dariel, In *11th Int. Conf. on CVD*, PV 90-12 (edited by K. E. Spear), p. 696. Electrochemical Society, Pennington, NJ (1990).
41. R. Moene, J. P. Dekker, M. Makkee, J. Schoonman and J. A. Moulijn, *J. Electrochem. Soc.* **141**, 282 (1994).
42. C. N. Satterfield, *Heterogeneous Catalysis in Practice*, 2nd edn. McGraw Hill, New York (1980).