

Oligomers with silicon and transition metal groups: thermolysis of poly[1,1'-bis(diorganosilylethynyl)ferrocenes] and poly[[(diorganosilylene) diacetylene] dicobalthexacarbonyls] to give iron silicide- and cobalt silicide-based ceramics

Robert J.P. Corriu, Nathalie Devylder, Christian Guerin^{*}, Bernard Henner^{*}, Alain Jean

Unité Mixte CNRS-Rhône-Poulenc-Université Montpellier II, Unité Mixte de Recherche au CNRS 44, Case courrier 007, Université Montpellier II, Sciences et Techniques du Languedoc, place E. Bataillon, F-34095 Montpellier Cédex 05, France

Received 26 May 1995

Abstract

The pyrolysis of transition-metal-containing organosilicon-diacetylene oligomers was performed in order to prepare multiphase ceramics. Poly[1,1'-bis(diorganosilylethynyl)ferrocenes] (**2**) were pyrolysed, under argon, up to 1350°C to give $Fe_xSi_yC_z$ phases with good yields, owing to the incorporation of the cyclopentadiene groups in the carbon matrix and the participation of nearly all silicon and iron in the ceramic residue. The pyrolysis of poly[[(diorganosilylene) diacetylene] dicobalt hexacarbonyls] (**3**) at 1350°C gave Co_2Si and graphite-like carbon. Evolution of part of the carbon monoxide of **3** in the early stage of the pyrolysis (100°C) showed that the cross-linking of the diacetylene units was induced by reactive cobalt species. Furthermore, at higher temperatures (200–500°C), cobalt clusters catalysed the ceramic formation. Co_2Si was shown to result from the reaction of SiC with Co above 1000°C, both formed during the pyrolysis process. Finally, at 1100°C, a carboreduction reaction led to the elimination of the oxygen incorporated in the carbon matrix during the cross-linking process.

Keywords: Poly[(silylene)diacetylenes]; Iron silicide; Multiphase ceramic; Pyrolysis; Cobalt silicide

1. Introduction

Silicon carbide is of particular interest because of its high thermal and chemical stability, low density, high mechanical strength and hardness, and high thermal conductivity [1]. These properties combine to make SiC attractive for use in multiphase ceramics of the type SiC–X and X being Si_3N_4 [2], TiB_2 [3], AlN [4], $MoSi_2$ [5] or TiC [6], which have been shown to have often superior properties compared with the component pure phases.

Such composite materials are in most cases prepared by the conventional method of high temperature, high pressure sintering. Although sintering is a common and well-established process for obtaining ceramics, its main disadvantage is the high processing temperature, promoting grain growth, thereby discouraging nanosized microstructures [1]. As an alternative, a chemical pro-

cessing route with an organometallic precursor to prepare Si–C– M_T phases (M_T = transition metal) can be envisaged. It offers several advantages including initiation of solid state reactions under milder conditions, and improved control over composition, microstructure and final form of the expected material [7]. With this aim, the introduction of a transition metal in a ceramic char can be performed in three different ways.

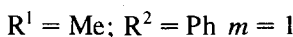
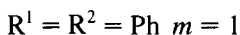
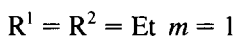
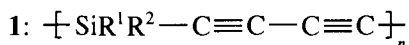
(i) The first approach, developed by Seyferth et al. [8], involves the pyrolysis of mixtures of pre-ceramic polymers (Nicalon polycarbosilane or polysilazane of the type $[(CH_3Si(H)NH)_a(CH_3SiN)_b]_n$ for instance) with commercial transition metal powders (Ti, Zr, V, Ni, Mo, W, etc.) in a stream of argon or ammonia. In the case of titanium and polycarbosilane, as an example, these workers obtained a mixture of SiC–TiC, carrying out the experiment under argon, or SiC–TiN in the case of the pyrolysis performed in a stream of ammonia. The same route was used by Jiang and Rhine [9] with vinyl polysilanes and boron or silicon.

(ii) A second route that we have developed consists

^{*} Corresponding authors.

of the pyrolysis of poly[(diorganosilylene)diacetylene]–metal oxide composites [10].

For example, polymer **1** with a regular alternating arrangement of silylene and diacetylene units [11] affords β -SiC-containing ceramics with high yields after pyrolysis in an argon stream [12]. The ceramic chars contain a large excess of free carbon coming from diacetylene units and from the groups attached to silicon.

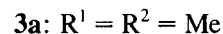
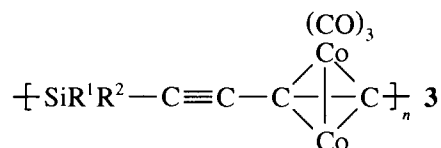
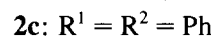
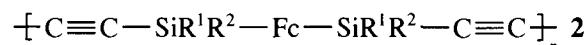


The controlling factor of the process is an efficient cross-linking through the triple bonds; the polymers are thermally converted into an amorphous matrix of sp^2 -hybridized carbon atoms, in which the SiC network is formed without loss of organosilicon compounds. The transmission electron microscopy (TEM) of the residue indicates that SiC is regularly dispersed in the carbon matrix with an average particle size of 2.5 nm [13]. Taking advantage of these properties, the poly[(silylene)diacetylenes] were used as “wrapping polymers” for metal oxides [10,14,15]. During the pyrolysis, the excess of carbon allowed the carboreduction of the encapsulated oxide particles and formation of silicon carbide–metal carbide ceramics of various and well-defined compositions when working in an argon stream [10]. The pyrolysis performed in a reactive atmosphere of dinitrogen gave efficient carboreduction and nitridation and led to silicon carbide–metal nitride ceramics [15]. Improvements are found when metal alkoxides are used as molecular sources of the corresponding oxides [16]. The ceramic particules exhibit an Si–M composition (as determined at the nanometric level by energy dispersive X-ray analysing) corresponding to mixed ceramic phases with interpenetrating networks [17].

(iii) Attention can also be directed towards the pyrolysis of organometallic polymers containing both organosilicon and metal groups in their structure. Indeed, the dispersion of the metal at the atomic level in the pre-ceramic organosilicon polymer as an organometallic moiety may control both the stoichiometry and the microstructure of the resultant ceramic [7b]. Organometallic complexes are known to decompose thermally at relatively low temperatures [18] and this must lead to the formation of metal clusters regularly dispersed in a carbon matrix. Aylett and coworkers [19], for instance, prepared transition metal silicides by thermal decomposition of organometallic complexes. Pyrolysis of poly(ferrocenyilsilanes) was used by Manners

and coworkers [20] to obtain iron silicide carbide ceramics.

Recently, our current interest in the design, synthesis and pyrolysis of precursors to SiC-containing ceramics [21] led us to prepare poly[(silylene)diacetylene]-type oligomers containing organometallic moieties [22]. This paper focuses on the thermal behaviour of such derivatives, namely **2a–2c** and **3a**, **3b** and their use as potential non-oxide ceramic precursors. Oligomers **2** contain 1,1'-ferrocenyl units in the main chain, while **3** corresponds to the complexation of one of the acetylenic units of **1** with $\text{Co}_2(\text{CO})_8$.

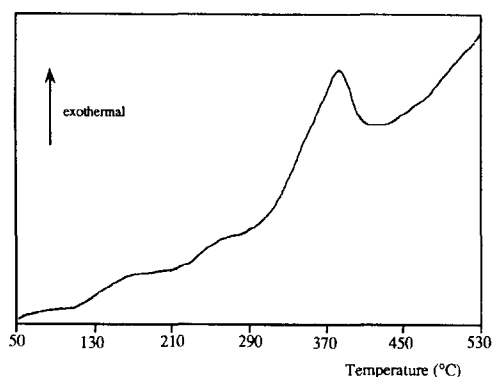
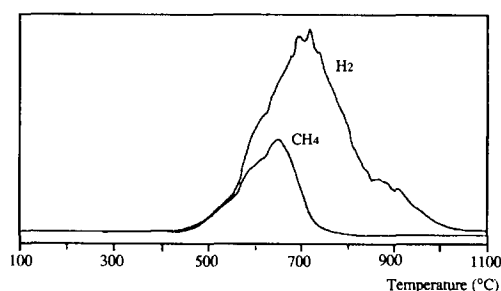


2. Results and discussion

2.1. Poly[1,1'-bis(diorganosilylethynyl)ferrocenes] (**2**)

The thermal transformations of oligomers **2a–2c** were analysed using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and thermodifferential analysis (TDA) in an atmosphere of argon. The results are summarized in Table 1. Fig. 1 gives the DSC curve for **2c**.

Oligomers **2a–2c** are powders and as observed previously in the case of the poly[(silylene)diacetylenes] [12], the DSC curves showed no melting point. Two (**2a**) or one (**2b** and **2c**) exotherms which correspond to the solid state cross-linking of the triple bonds were detected. These exotherms are very broad indicative of a slow cross-polymerization reaction and occurred at higher temperatures (mainly 350–390°C) than in the case of poly[(dimethylsilylene)diacetylene] (200°C). The enthalpies of the processes are also smaller, $70 \text{ J g}^{-1} \leq \Delta H \leq 160 \text{ J g}^{-1}$, vs. $\Delta H = 755 \text{ J g}^{-1}$. The polymerization process is more difficult because these oligomers are amorphous, as demonstrated by their powder X-ray diffractograms. Indeed, we have shown previously with poly[(silylene)diacetylenes] that the cross-polymerization through the triple bonds depended greatly on the crystallinity of the starting material which is connected to the steric requirements of the substituents bonded at

Fig. 1. DSC curve of **2c**.Fig. 2. Pyrolysis of **2a** to 1100°C, under argon: mass spectrum traces.

silicon [23]. On this basis, the presence of an additional small exotherm centred at 223°C in the case of the less-hindered oligomer **2a** would be the result of the presence of small crystalline zones, where an easier polymerization process starts and, at higher temperatures extends to the whole mass of the material.

Oligomers **2a–2c** were pyrolysed at 10°C min⁻¹ up to 1350°C with a hold of 4 h at that temperature. In both cases, the TGA curves showed that the weight loss occurred in one step, mainly between 400 and 800°C (Table 1). The ceramic residues were obtained with high yields (74.5–84.5%) owing to the efficient cross-linking through the triple bonds. The general appearance of the ceramic char corresponded to a black residue with small metallic-like particles. Elemental analysis of the residues gave iron, silicon, carbon and small amounts of oxygen. The silicon-to-iron ratio corresponded to 2 to 1, i.e. the ratio in the starting oligomers. Table 1 indicates also that all iron and silicon present in the starting oligomers **2a–2c** were recovered in the ceramic residues. The amount of carbon in the residue was large (**2a**, 60.7%; **2b**, 64.5%; **2c**, 73.3%) and indicated that the major part of the carbons of both the cyclopentadi-

enyl groups and the substituents at silicon are incorporated into the carbon matrix; indeed, the carbon content was greater with phenyl than with methyl substituents, as outlined previously in the case of poly[(silylene)diacetylenes] [12]. It must be emphasized that in the case of the pyrolysis of poly(ferrocenyl silanes) in a stream of nitrogen, ceramic yields of only 35–40% were indicative of the loss of most of the cyclopentadienyl ligands present in the starting polymer [20]. This result stresses again the important influence of the diacetylene units in the pyrolysis process.

X-ray powder diffractograms of the ceramics obtained from oligomers **2a–2c** are similar: β-SiC and Fe_xSi_yC_z phases were observed. Owing to a great number of phases corresponding to Fe and Si, Fe and C or Fe, Si and C, it was not possible to assign unambiguously the X-ray diffraction peaks. Also, the very hard metallic-like particles have not been characterized.

In the case of the pyrolysis of the dimethylsilyl oligomer **2a**, the off-gases of the thermolysis were analysed by mass spectrometry (Fig. 2). As expected, methane was observed between 450 and 750°C and hydrogen evolved from 450 up to 1000°C with a maximum around 700°C. No evolution of cyclopentadiene was observed.

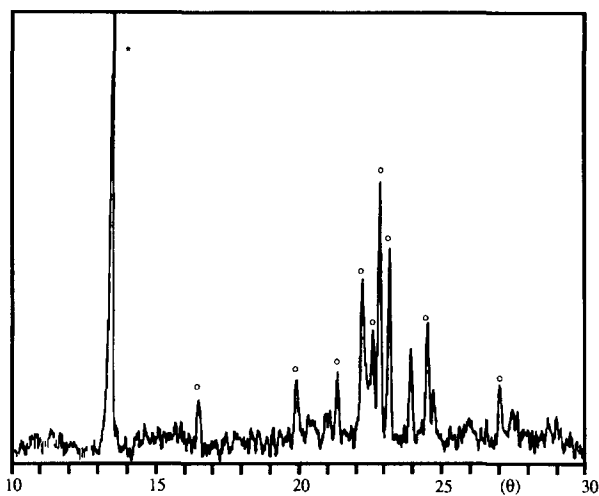
Table 1
Thermal behaviour of poly[1,1'-bis(diorganosilylethynyl)ferrocenes] (**2**)

	R	R'	TGA weight loss (temperature range)	TDA	DSC	Analysis ^a (empirical formula)	Amount recovered ^c	
							Si	Fe
2a	Me	Me	Δm = 15.5% (450–800°C)	340°C	2 exotherms 223°C ΔH = 8 J g ⁻¹ 344°C ΔH = 110 J g ⁻¹	C, 60.72; Si, 18.55; Fe, 18.81; O, 1.68 (C ₁₅ FeSi ₂ O _{0.35})	97%	99%
2b	Me	Ph	Δm = 25.5% (400–800°C)	350°C	350°C ΔH = 160 J g ⁻¹	C, 64.48; Si, 12.34; Fe, 12.10; O, 3.87 (C _{24.4} FeSi ₂ O ₁)	^b	^b
2c	Ph	Ph	Δm = 21.5% (450–800°C)	375°C	390°C ΔH = 69 J g ⁻¹	C, 73.31; Si, 11.54; Fe, 12.49; O, 2.13 (C _{27.4} FeSi _{1.85} O _{0.6})	96%	100%

^a Residue pyrolysed at 1350°C.

^b Not calculated because the sum of the individual percentages accounts for 93% of the expected value.

^c Calculated from elemental analysis and pyrolysis yield ρ. As an example, %Si recovered = (%Si_{res} × ρ) / %Si_{pre}, where %Si_{res} is the percentage of silicon in the residue and %Si_{pre} is the percentage of silicon in the precursor.



Indexation: * C; ° Co₂Si

Fig. 3. Powder X-ray diffractogram of **3b** pyrolysed at 1400°C, under argon.

The general behaviour of the pyrolysis of the poly[1,1'-bis(diorganosilylethynyl)ferrocenes] (**2a–2c**) is very similar to that observed in the case of poly[(diorganosilylene)diacetylenes], i.e. firstly cross-linking in the solid state through the triple bonds without weight loss giving the formation of a carbon matrix with SiR₂ groups, and secondly ceramic formation with incorporation of the carbon from the cyclopentadienyl ligands in the carbon matrix and formation of SiC and Fe_xSi_yC_z phases.

2.2. Dicobalthexacarbonyl complexes of poly[(diorganosilylene)diacetylenes]

2.2.1. Bulk pyrolysis

Oligomers **3a** and **3b** with one of the triple bonds complexed with dicobalt hexacarbonyl [22] were pyrolysed up to 1400°C under an inert atmosphere of argon. Table 2 gives the ceramic yields, elemental analyses and the powder X-ray analysis of the residues.

The yields of the ceramic residues from **3a** and **3b** were found to be around 50%; these are reasonable yields if we consider that the carbonyl groups are very labile ligands and represent 37% (**3b**) and 43% (**3a**) of

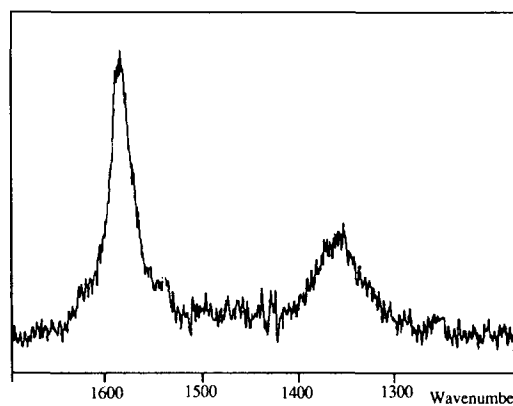


Fig. 4. Raman spectrum of **3a** pyrolysed at 1400°C, under argon.

the weight of the starting oligomers. Elemental analysis gave silicon and cobalt in a nearly 1:2 stoichiometry; carbon was also present. These facts and the ceramic yields obtained indicated that, during pyrolysis, nearly all the silicon and cobalt was recovered (see Table 2). X-ray analysis indicated the formation of Co₂Si and organized carbon ($\theta = 13.28^\circ$). No crystallized β -SiC was observed in the X-ray diffractogram. As an example, Fig. 3 gives the X-ray trace of the ceramic residue obtained from **3b**.

Raman spectroscopy is known to be a suitable method for characterizing poorly crystallized solids and, for instance, amorphous and graphitic carbon. Two peaks are observed: one around 1350 cm⁻¹ (disorder-induced line) and the second near 1580 cm⁻¹ (Raman allowed graphite-like E_{2g} mode) [24]. The Raman spectrum of pyrolysed **3a** (Fig. 4) showed a broad peak at 1359 cm⁻¹ and a relatively sharp peak at 1580 cm⁻¹. The major part of the carbon is in graphite-like form; a small peak at 1553 cm⁻¹ confirmed that the graphitization of the carbon was not complete. Some information can be gained about the domain size and the relative order or disorder of the graphitic carbon [25]; the D (1357 cm⁻¹)-to-G (1580 cm⁻¹) intensity ratio I_D/I_G is 0.33 and the G bandwidth is close to 30 cm⁻¹. This corresponds to an average domain size of 100–150 Å and an ordering similar to polycrystalline graphite [25b].

The formation of Co₂Si can be envisaged as involv-

Table 2
Thermal behaviour of poly[[(silylene)diacetylene]dicobalthexacarbonyls] (**3**)

	R	R'	ρ	Analysis (empirical formula)	Amount recovered ^a		X-ray
					Si	Co	
3a	Me	Me	51%	C, 23.70; Si, 15.01; Co, 60.89; O, 0.52 (C _{3.7} Si ₁ Co _{1.9} O _{0.06})	92%	89%	Co ₂ Si
3b	Me	Ph	53%	C, 38.02; Si, 10.60; Co, 39.81; O, 0.72 (C _{8.4} Si ₁ Co _{1.8} O _{0.1})	^b	^b	C _{graph} Co ₂ Si C _{graph}

^a Calculated from elemental analysis and pyrolysis yield ρ . As an example: %Si recovered = (%Si_{res} × ρ)/%Si_{pre} where %Si_{res} is the percentage of silicon in the residue and %Si_{pre} is the percentage of silicon in the precursor.

^b Not calculated because the sum of the individual percentages accounts for 89.15%.

ing the reaction of cobalt with SiC [26]. Oligomers **3a** and **3b** were pyrolysed up to 800°C and the residues analysed by powder X-ray diffraction and IR spectrometry. The latter technique gave the characteristic band of SiC at 860 cm⁻¹, whereas the powder X-ray diffractogram indicated no crystalline phase at that temperature. When pyrolysed to 1000°C for 1 h, under argon, the X-ray diffractogram of **3a** gave the sharp lines of cobalt metal. Thus the formation of Co₂Si can be explained by the reaction of finely dispersed cobalt metal with amorphous SiC dispersed in carbon at a temperature above 1000°C.

Pyrolysis of poly{[(dimethylsilylene)diacetylene] dicobalt hexacarbonyl} led to a ceramic composed of Co₂Si and graphite-like carbon. To study the influence of the cobalt on the process, we pyrolysed poly{[(dimethylsilylene)diacetylene] complexes with a different dicobalt hexacarbonyl content and also a mixture of poly{[(dimethylsilylene)diacetylene] and commercial cobalt metal (Table 3). When only 30% of the diacetylene units were complexed with Co₂(CO)₈ (Table 3, entry 2), the pyrolysis up to 1350°C under an inert atmosphere of argon gave a 56% ceramic yield. Elemental analysis indicated that carbon, silicon and nearly all the cobalt introduced in the polymer were recovered in the final ceramic. X-ray analysis of the residue gave CoSi, SiC and graphite-like carbon. As expected from the cobalt-to-silicon stoichiometry in the starting complexes, CoSi was favoured over Co₂Si when the Co-to-Si ratio was decreased. The influence of cobalt on the process was also studied with cobalt metal (Table 3, entry 3). Commercial cobalt metal powder (100 mesh) was dispersed in a solution of poly{[(dimethylsilylene)diacetylene] in tetrahydrofuran (THF) and the solvent removed under vacuum. The pyrolysis of the solid obtained first leads to polymerization through the triple

bonds: encapsulation of cobalt in a carbon matrix, as observed in the case of metal oxides [10,15], would favour the contact with the metal during the pyrolysis process. This reaction was performed with a silicon-to-cobalt ratio of 1 to 2 (Table 3, entry 3). After pyrolysis to 1350°C, graphitic carbon and cobalt metal were observed in the X-ray diffractogram. CoSi, Co₂Si SiC were not detected; however, the amount of cobalt metal and its grain sizes (150 μm), led to very broad peaks in the X-ray diffractogram, which make the detection of other species difficult. Thus, if a reaction takes place between the micron-scale metal powder and the carbon matrix derived from cross-linking of the poly{[(dimethylsilylene)diacetylene]}, the transformation is quite slow. In sharp contrast, the pyrolysis of **3a**, in which finely dispersed in-situ-generated cobalt is involved, gives rise to complete formation of Co₂Si under similar conditions.

2.2.2. Thermal analysis and mechanism.

To obtain more information, the pyrolysis to 1000°C, under an argon atmosphere, of the cobalt complex **3a** was studied by TGA and the off-gases were analysed by mass spectrometry (Fig. 5).

The TGA curve of **3a** showed that the weight loss (34%) occurred in one step, mainly from 150 to 350°C. Three, nearly successive gas evolutions were observed: from 100 to 300°C, with a maximum intensity at 200°C, carbon monoxide was observed; methane evolution started near 200°C with a maximum intensity close to 350°C; finally, hydrogen was detected from 300 to 1000°C. The observed weight loss of 34% is smaller than the expected value of 47.5% based on the stoichiometry of **3a** and an ideal SiCo₂C₅ composition (the pyrolysis of poly{[(dimethylsilylene)diacetylene] leads to SiC₅). The data suggest that carbonyl groups are incor-

Table 3
Pyrolysis^a of poly{[(dimethylsilylene) diacetylene] alone, with 30% of the diacetylene units complexed with Co₂(CO)₈ and with cobalt metal

Entry	Precursors	ρ ^b	Analysis (Empirical formula)	X-ray
1	$\text{-(SiMe}_2\text{-C}\equiv\text{C-C}\equiv\text{C)}_n\text{-}$ ^c	84%	(C ₅ Si)	SiC
2	$\text{-(SiMe}_2\text{-C}\equiv\text{C-C}\equiv\text{C)}_7\text{-}$ $\text{-(SiMe}_2\text{-C}\begin{array}{c} \text{(CO)}_3 \\ \diagup \text{Co} \diagdown \\ \\ \text{C} \\ \\ \text{C} \\ \diagdown \text{Co} \diagup \\ \text{(CO)}_3 \end{array}\text{-C}\equiv\text{C)}_3\text{-}$	56%	C, 46.93; Si, 20.97; Co, 25.70; O, 1.15 (C _{4.5} Si _{0.9} Co _{0.5} O _{0.08})	CoSi, SiC C _{graph} ^d
3	$\text{-(SiMe}_2\text{-C}\equiv\text{C-C}\equiv\text{C)}_n\text{-}$ + 2nCo	89%	C, 25.08; Si, 10.77; Co, 54.07; O, 0.43 (C _{4.2} Si _{0.77} Co _{1.8} O _{0.05})	C _{graph} Co _{metal}

^a Up to 1350°C.

^b Pyrolysis yield.

^c See [11].

^d Small amounts.

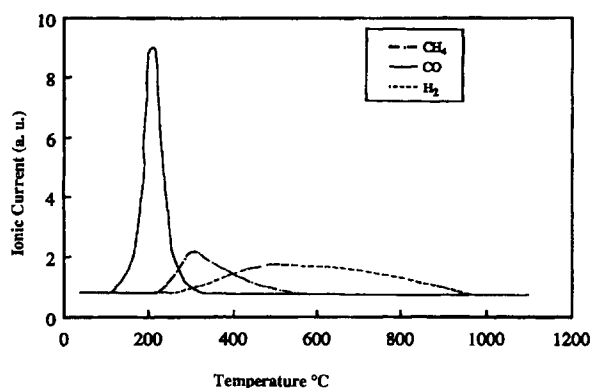


Fig. 5. Pyrolysis of **3a** to 1000°C under argon: mass spectrum traces (a.u. arbitrary units).

porated during the pyrolysis. For instance, incorporation of two carbonyls in the carbon matrix during the initial stages would lead to 33.1% weight loss, close to the experimental value. Furthermore, when the pyrolysis was continued to 1300°C, a second weight loss, identified as carbon monoxide by mass spectrometry (Fig. 6), was observed; this loss (15%) corresponded to the evolution of 2 mol of carbon monoxide, if we assume that all the cobalt and silicon are recovered in the residue. The total weight loss of 49% gave a residue which, formally, corresponds to Co_2Si , 4.5C.

Oligomer **3a** and poly[(dimethylsilylene)diacetylene] show quite different thermal behaviours under the same conditions (i.e. 1000°C, an argon atmosphere and a heating rate of $10^\circ\text{C min}^{-1}$). In the latter case, the mineralization starts about 200°C above the temperature observed for **3a**. The weight loss occurred in one step between 400 and 700°C. Methane evolved from 400 to 700°C with a maximum near 600°C; hydrogen evolution started as around 500 up to 900°C with a maximum near 600°C [12]. Furthermore, no carboreduction takes place at higher temperature. Thus the data clearly show the

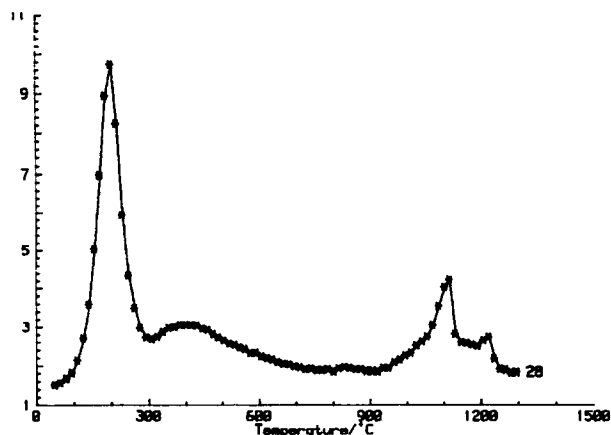


Fig. 6. Pyrolysis of **3a** to 1300°C, under argon. Mass spectrum trace of the carbon monoxide evolution.

influence of the [cobalt carbonyl] moieties in the pyrolysis process.

From a mechanistic point of view, the following comments can be made.

(i) Thermal cross-linking of poly[(silylene)diacetylene] through the triple bonds occurs at 200°C, via a 1,4-addition mechanism which leads to the formation of butatriene and eneyne units. The latter are converted at higher temperatures into an amorphous C sp^2 matrix [12]. In the case of their cobalt-complexed analogues **3a** and **3b**, the cross-polymerization step follows a quite different process. Evolution of carbon monoxide is observed in the early stage of the pyrolysis (100°C for **3a**); this elimination will result in the formation of organometallic cobalt clusters attached to the triple bonds of the oligomeric structure. Such species can be involved in the generation of reactive cobaltacycles and (cyclobutadiene)cobalt derivatives [27]. Indeed, cobalt complexes are known to give easily metallacycles which are invoked as intermediates in the cyclotrimerization of alkynes [28]. Thus the in-situ generation of such species will lead to an unsaturated carbon matrix pre-figuring the graphite-like structure observed at the end of the pyrolysis. Furthermore, the formation of (η^4 -cyclopentadienone)cobalt-type species can also be invoked to explain the incorporation of carbon monoxide in the carbon backbone; indeed, the reaction of 1,4-bis(trimethylsilyl)-1,3-butadiyne with $\text{CpCo}(\text{CO})_2$ led to the formation of a mixture of several compounds, among which two isomeric (η^4 -cyclopentadienone)(η^5 -cyclopentadienyl)cobalt compounds were the major products [28a].

(ii) The presence of cobalt species results in a significant lowering of the temperature range in which the ceramic formation step takes place. Indeed, in the case of **3a**, methane was evolved from 200 to 500°C, and hydrogen from 300 up to 1000°C. Scheme 1 gives a possible mechanism for the ceramic formation of **3a**.

The most probable primary process corresponds to the insertion of [Co] units into a C–H bond [28] ([Co] represents an organometallic cobalt species formed from the thermal degradation of the (alkyne) $\text{Co}_2(\text{CO})_6$) (Scheme 1(a)). Further decomposition (the thermal degradation of cobalt alkyls is known to be very easy [18]) will lead to the stabilized silylmethyl radical **4** and concomitant release of a hydrogen radical (Scheme 1(b)). Compound **4** is part of a highly cross-linked carbon matrix which prevents it from moving away from the other reactive centers present in the solid. Thus direct attack of **4** at a neighbouring silicon centre is postulated as a propagation step (Scheme 1(c)). It should correspond to the formation of a framework composed of methylene moieties ($\text{Si-CH}_2\text{-Si}$) and release of a methyl radical. The latter may abstract hydrogen from C–H bonds and regenerate **4** with evolution of methane (Scheme 1(d)). In other words, the above reactions

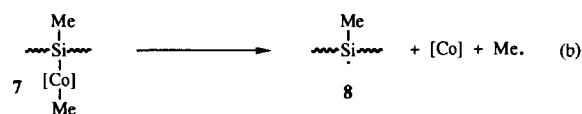
would lead to the stepwise conversion of the isolated dimethylsilyl groups into a $[-Si-CH_2-]$ polycarbosilane backbone **5** inside the carbon matrix containing cobalt. Moreover, it explains the evolution of methane in the initial stages of the mineralization process between 200 and 500°C. In the later stages, the major component of the volatile species becomes H_2 . At that time, the material is progressively converted into an inorganic structure. These changes will include (i) the homolysis of the remaining C–H bonds (species such as **6** can be invoked (Scheme 1(e)), the cross-linking by radical recombinations, and thus consolidation of the “SiC” network and (ii) the scission of the Si–C matrix bonds with formation of free carbon (Scheme 1(f) and Scheme 1(g)).

An alternative process, certainly less likely, is the less usual insertion of a transition metal moiety into a silicon-carbon bond [29] (Scheme 2(a)). Further reaction would give rise to the silyl radical **8** and a methyl radical (Scheme 2(b)). The latter will continue the

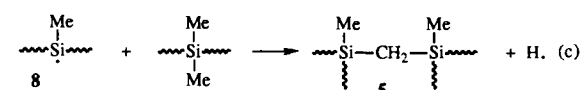
Insertion



Initiation



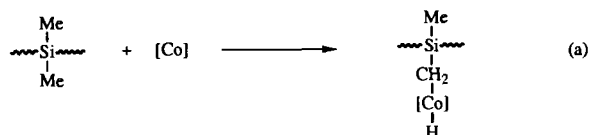
Propagation



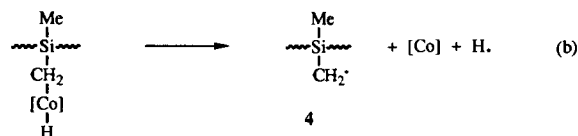
--- = carbon matrix resulting from the cross-linking process

Scheme 2.

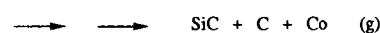
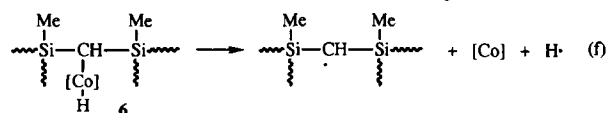
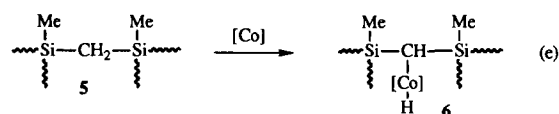
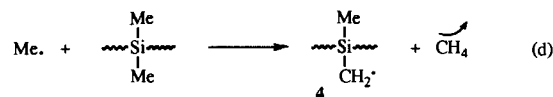
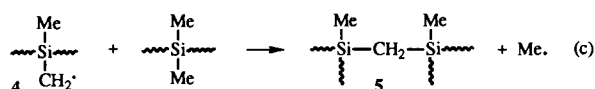
Insertion



Initiation of the mineralization



Propagation of the mineralization



--- = carbon matrix resulting from the cross-linking process

Scheme 1.

propagation process according to Scheme 1(d). Compound **8** may be involved in the formation of the $[-Si-CH_2-Si-]_n$ framework; **5** (Scheme 2(c)) and **4** may be obtained by reaction with a hydrogen radical (Scheme 2(d)).

(iii) At temperatures above 1000°C, the cobalt clusters will act as very reactive species towards the amorphous SiC present in the carbon matrix and will lead easily to the generation of Co_2Si . Furthermore, we did not observe the formation of Co_2Si when a mixture of poly[(dimethylsilylene)diacetylene]-cobalt powder (100 mesh) was pyrolysed under similar conditions. The same feature, i.e. the high reactivity of the in-situ-generated cobalt clusters, explains the efficient organization of carbon into a graphitic-like structure. Indeed, the conversion of amorphous carbon into graphitic carbon is known to be catalysed by transition metals [30].

(iv) As outlined above, the decomposition of cyclic unsaturated ketones species such as $(\eta^4\text{-cyclopentadienone})\text{cobalt}$, generated in the very initial stage of the thermal process would lead to incorporation of carbon monoxide in the carbon backbone. As a consequence, the presence of oxygen in the material results in a partial oxidation of reactive cobalt or silicon species formed during the pyrolysis and finally, at temperatures above 1100°C, carboreduction occurred with evolution of carbon monoxide.

3. Conclusion

We have found that pyrolysis of organometallic oligomers containing a transition metal group is an efficient route for preparing Si–M–C multiphase ceramics. The introduction of ferrocene in the chain of

poly[(silylene)diacetylenes] allowed the formation of $Fe_xSi_yC_z$ phases with good yields by pyrolysis at 1350°C in an argon stream. The pyrolysis of poly[[(diorganosilylene)diacetylene]dicobalt hexacarbonyls] (**3**) at 1350°C gave Co_2Si and graphite-like carbon. The formation of Co_2Si was found to occur from reaction of cobalt metal with silicon carbide, both being formed during the decomposition process. When compared with its non-complexed oligomer analogue, **3a** showed that both cross-linking and ceramic formation steps occurred at lower temperatures (lower by 100 and 200°C respectively). This clearly indicates the participation of cobalt species during these two steps; these entities may be cobaltacycles in the cross-linking process and cobalt alkyls (or aryls) or hydrides during mineralization. The regularly dispersed cobalt clusters may explain the efficient organization of carbon into graphite-like carbon.

4. Experimental section

All reactions were carried out under nitrogen using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. THF was distilled over sodium-benzophenone.

Cobalt octacarbonyl was purchased from Strem Chemicals. The synthesis of the following compounds were published previously: poly[1,1'-bis(diorganosilyl-ethynyl) ferrocenes] (**2**) [22], poly[[(diorganosilylene)diacetylenes]dicobalthexacarbonyl] (**3**) [22], poly[(dimethylsilylene)diacetylene] [11].

All NMR measurements were obtained at ambient temperature. 1H spectra were acquired by using a Bruker AW 80 instrument and ^{13}C and ^{29}Si solution spectra with a Bruker WP 200 SY or WP 250 AC spectrometers. Chemical shift data were referenced to tetramethylsilane (TMS).

4.1. Synthesis of poly[(dimethylsilylene) diacetylene] with 30% of the diacetylene units complexed with $Co_2(CO)_8$

The same procedure as for the synthesis of poly[[(diorganosilylene)diacetylenes]dicobalt hexacarbonyl] (**3**) was used [22]. A solution of dicobalt octacarbonyl (2.26 g, 0.0066 mol) in THF (10 ml) was added to a solution of poly[(dimethylsilylene)diacetylene] (2.34 g) in the same solvent (30 ml). Gas evolution was observed. After stirring for 12 h, the volatiles were eliminated under vacuum and the residue was washed with pentane to give a brown viscous oil (4.15 g) with a quantitative yield. IR (THF, cm^{-1}): $\nu(C\equiv O)$ 2092, 2060, 2029; $\nu(C\equiv C)$ 2079 cm^{-1} .

4.2. Thermal analyses

Argon (O_2 , less than 5 ppm; H_2O , less than 5 ppm) was used as the inert gas for the TGA experiments and

the thermal decomposition reactions. IR spectra were recorded with a Perkin–Elmer 1600 FT spectrometer operating at 4 cm^{-1} resolution. Solid IR samples were prepared under a normal atmosphere as KBr pellets. Elemental analyses were performed by the Centre de Microanalyse du CNRS. X-ray diffraction measurements were obtained using Cu $K\alpha$ radiation with a Philips diffractometer.

Simultaneous TGA–TDA were performed under flowing argon (50 ml min^{-1}) with a Netzsch STA 409 thermobalance interfaced with an Anagas 200 Delsi-Nermag mass spectrometer through a capillary tube and a molecular leak. The typical heating rate was 10°C min^{-1} .

DSC experiments were performed on a Mettler 30 instrument under argon at a heating rate of 5°C min^{-1} .

The pyrolysis experiments were performed by pouring weighed portions (0.1–1 g) of the oligomer into an aluminium oxide boat (80 mm \times 10 mm \times 10 mm) which was placed into a gas-tight aluminium oxide tube (1 m; inside diameter, 30 mm) fitted with glass taps to allow connection to a vacuum line. During pyrolysis, the argon flow was maintained around 50 ml min^{-1} . Pyrolyses were performed with an Eurotherm or Carbolite furnace, using a temperature program as given in the text.

Acknowledgement

The authors thank Dr. P.V. Huong, Laboratoire de Spectroscopie Moléculaire et Cristalline, Unité de Recherche associée au CNRS 124, Université de Bordeaux 1, 351 cours de la Libération, 33405 Talence Cedex, France, for the Raman spectrum measurements and interpretation.

References and notes

- [1] M. Touanen, F. Teyssandier, M. Ducarroir, M. Maline, R. Hillel and J.L. Derep, *J. Am. Ceram. Soc.*, **76** (1993) 1473.
- [2] (a) F.F. Lange, *J. Am. Ceram. Soc.*, **56** (1973) 445; (b) D. Seyferth and G.H. Wiseman, *J. Am. Ceram. Soc.*, **67** (1984) C132; (c) T. Buljan, J.G. Baldoni and M.L. Huckabee, *Am. Ceram. Soc. Bull.*, **66** (1987) 347; (d) G.E. Legrow, T.F. Lim, J. Lipowitz and R.S. Reaach, *Am. Ceram. Soc. Bull.*, **66** (1987) 363.
- [3] M. Janney *Am. Ceram. Soc. Bull.*, **66** (1987) 322.
- [4] (a) M. Landon and F. Thevenot, *Ceram. Int.*, **17** (1991) 97; (b) W.C.J. Wei and R.R. Lee, *J. Mater. Sci.*, **26** (1991) 2930; (c) L.V. Interrante, W.R. Schmidt, S.N. Shaikh, R. Garcia, P.S. Marchetti and G.E. Maciel, in L.L. Hench and J.K. West (eds.), *Chemical Processing of Advanced Materials*, Wiley, New York, 1992; (d) J.-F. Li and R. Watanabe, *J. Mater. Sci.*, **26** (1991) 4813.
- [5] A.K. Bhattacharya and J.J. Petrovic, *J. Am. Ceram. Soc.*, **74** (1991) 2700.
- [6] (a) G.C. Wei and P.E. Becher, *J. Am. Ceram. Soc.*, **67** (1984) 571; (b) M.A. Janney, *Am. Ceram. Soc. Bull.*, **65** (1986) 357.

- [7] (a) L.V. Interrante, W.R. Schmidt, P.S. Marchetti and G.E. Maciel, *Materials Research Society Symp. Proc.*, Vol. 271, Material Research Society Pittsburgh, PA, 1992, p. 739, and references cited therein; (b) R.W. Chorley and P.W. Lednor, *Adv. Mater.*, 3 (1991) 474, and references cited therein.
- [8] (a) D. Seyferth, N. Bryson, D.P. Workman and C.A. Sobon *J. Am. Ceram. Soc.*, 74 (1991) 2687; (b) D. Seyferth, H. Lang, C.A. Sobon, J. Borm, H.J. Tracy and N. Bryson, *J. Inorg. Organomet. Polym.*, 2 (1992) 59.
- [9] Z. Jiang and W.E. Rhine, *Materials Research Society Symp. Proc.*, Vol. 286, Materials Research Society, Pittsburgh, PA, 1993, p. 437, *Chem. Abstracts*, 119, (1993) 277203.
- [10] R. Corriu, Ph. Gerbier, C. Guérin and B. Henner, *Angew. Chem., Int. Edn. Engl.*, 31 (1992) 1195.
- [11] (a) R. Corriu, C. Guérin, B. Henner, A. Jean and T. Kuhlmann, *Fr. Pat. A 05567*, 1989; (b) R. Corriu, C. Guérin, B. Henner, A. Jean, F. Garnier and A. Yassar *Chem. Mater.*, 2 (1990) 351; (c) J.L. Bréfort, R. Corriu, C. Guérin, B. Henner, A. Jean, F. Garnier and A. Yassar, *Organometallics*, 11 (1992) 2500.
- [12] (a) R. Corriu, C. Guérin, B. Henner, A. Jean and P.H. Mutin *J. Organomet. Chem.*, 396 (1990) C35; (b) R. Corriu, C. Guérin, B. Henner, A. Jean and P.H. Mutin, *Organometallics*, 11 (1992) 2507; (c) A. Jean, *Ph.D. Thesis*, Université de Montpellier II, 1991.
- [13] R.J.P. Corriu, Ph. Gerbier, C. Guérin and B. Henner, in preparation.
- [14] The polymer–metal oxide route was used in the case of metal borides: (a) K. Su and L.G. Sneddon, *Chem. Mater.*, 3 (1991) 10. (b) K. Su and L.G. Sneddon, *Chem. Mater.*, 5 (1993) 1659.
- [15] R. Corriu, Ph. Gerbier, C. Guérin and B. Henner, *Adv. Mater.*, 5 (1993) 380.
- [16] See for instance: (a) S. Yajima, T. Inai, T. Yamamura, K. Okanamura and H. Hagesawa, *J. Mater. Sci.*, 16 (1981) 1349; (b) T. Yamamura, Y. Ishikawa, M. Shibuya, T. Hisayuki and K. Okamura, *J. Mater. Sci.*, 23 (1988) 2589; (c) Y.-C. Song, Y. Hagesawa, S.J. Yang and M. Sato, *J. Mater. Sci.*, 23 (1988) 1911; (d) F. Babonneau, G.D. Sorarù and J.D. Mackensie, *J. Mater. Sci.*, 25 (1990) 3664; (e) G.D. Sorarù, A. Glisenti, G. Granozzi, F. Babonneau and J.D. Mackensie, *J. Mater. Res.*, 5 (1990) 1958; (f) F. Babonneau, J. Livage, G.D. Sorarù, G. Carturan and J.D. Mackensie, *New J. Chem.*, 14 (1990) 539; (g) Y. Hagesawa, C.-X. Feng, Y.-C. Song and Z.-L. Tan, *J. Mater. Sci.*, 26 (1991) 3657.
- [17] R. Corriu, Ph. Gerbier, C. Guérin and B. Henner, in preparation.
- [18] See for instance: (a) F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* Wiley, New York, 4th edn., 1980; (b) H.D. Hutton, N.C. Pocard, D.C. Alsmeyer, O.J.A. Schueller, R.J. Spontak, M.E. Huston, W. Huang, R.L. McCreery, Th.X. Neenan and M.R. Callstrom, *Chem. Mater.*, 5 (1993) 1727.
- [19] (a) B.J. Aylett and H.M. Colquhoun, *J. Chem. Soc., Dalton Trans.*, (1977) 2058; (b) D.G. Anderson, N. Anwar, B.J. Aylett and I.S. Harding, *10th Int. Symp. on Organosilicon Chem., Poznan, 15–20 August 1993*.
- [20] (a) B.-Z. Tang, R. Petersen, D.A. Foucher, A. Lough, N. Coombs, R. Sodhi and I. Manners, *J. Chem. Soc., Chem. Commun.*, (1993) 523; (b) I. Manners, *J. Inorg. Organomet. Polym.*, 3 (1993) 185.
- [21] (a) R. Corriu, D. Leclercq, P.H. Mutin, J.M. Planeix and A. Vioux, *Organometallics*, 12 (1993) 454; (b) R. Corriu, D. Leclercq, P.H. Mutin and A. Vioux, *Chem. Mater.*, 4 (1992) 711; (c) B. Boury, R.J.P. Corriu and W. Douglas, *Chem. Mater.*, 3 (1991) 487; (d) B. Boury, L. Carpenter, R.J.P. Corriu and H. Mutin, *New J. Chem.*, 14 (1990) 535; (e) B. Boury, L. Carpenter and R.J.P. Corriu, *Angew. Chem., Int. Edn. Engl.*, 29 (1990) 785; (f) R.J.P. Corriu, W.E. Douglas and Z.X. Yang, *J. Polym. Sci., Polym. Lett. Edn.*, C, 28 (1990) 431; (g) A. Albizane, R.J.P. Corriu, W.E. Douglas and H. Fisch, *Polym. Int.*, 26 (1991) 93; (h) R.J.P. Corriu, W.E. Douglas, E. Layher and R. Shankar, *J. Inorg. Organomet. Polym.*, 3 (1993) 129; (i) D. Brondani, R.J.P. Corriu, S. El Ayoubi, J. Moreau and M. Wong Chi Man, *Tetrahedron Lett.*, 34 (1993) 2111; (j) R.J.P. Corriu, W.E. Douglas and Z.X. Yang, *J. Organomet. Chem.*, 455 (1993) 35; (k) R.J.P. Corriu, W.E. Douglas and Z.X. Yang, *J. Organomet. Chem.*, 456 (1993) 69.
- [22] R. Corriu, N. Devylder, C. Guerin, B. Henner and A. Jean, *Organometallics*, 13 (1994) 3194.
- [23] R. Corriu, Ph. Gerbier, C. Guérin, B. Henner and R. Fourcade, *J. Organomet. Chem.*, 449 (1993) 111.
- [24] See for instance: (a) E. Bouillon, R. Paillet, R. Naslain, E. Bacqué, J.-P. Pillot, M. Birot, J. Dunogues and P.V. Huong, *Chem. Mater.*, 3 (1991) 356; (b) Y. Sato, M. Kasuo and N. Setaka, *Carbon*, 16 (1978) 279; (c) M. Monthieux, A. Oberlin and E. Bouillon, *Comput. Sci. Technol.*, 37 (1990) 21.
- [25] (a) G.T. Burns, R.B. Taylor, Y. Xu, A. Zangvil and G.A. Zank, *Chem. Mater.*, 4 (1992) 1313; (b) D.S. Knight and W.B. White, *J. Mater. Res.*, 4 (1989) 385.
- [26] T.C. Chou, A. Joshi and J. Wadworth, *J. Mater. Res.*, 6 (1991) 796.
- [27] J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.
- [28] See for instance: (a) J.R. Fritch and K.P.C. Vollhardt, *Organometallics*, 1 (1982) 590; (b) B.C. Berris, G.H. Hovakeemian, Y.-H. Lai, H. Mestdagh and K.P.C. Vollhardt, *J. Am. Chem. Soc.*, 107 (1985) 5670; (c) M. Hirthammer and K.P.C. Vollhardt, *J. Am. Chem. Soc.*, 107 (1986) 2481; (d) R. Diercks and K.P.C. Vollhardt, *J. Am. Chem. Soc.*, 108 (1986) 3150; (e) L. Blanco, H.E. Helson, M. Hirthammer, S. Spyronidis and K.P.C. Vollhardt, *Angew. Chem., Int. Edn. Engl.*, 26 (1987) 1246.
- [29] U. Schubert, *Angew. Chem., Int. Edn. Engl.*, 33 (1994) 419.
- [30] See for instance: W.L. Holstein, R.D. Moorhead, H. Poppa and M. Boudart, *Chem. Phys. Carbon*, 18 (1982) 140, and references cited therein.