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Mass Spectrometric Study of the Gas Phase During Chemical Vapor Deposition of Pyrolytic Carbon

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Abstract. The pyrolysis of CH_4 , of C_3H_8 and of the mixture $20\text{C}_3\text{H}_8/80\text{CH}_4$ was investigated in a hot wall CVD reactor by mass spectrometry. Experiments were conducted as a function of temperature and of surface-to-volume (S/V) ratio of the substrate. The main by-products of the pyrolysis were identified and reaction mechanisms were proposed taking into account homogenous decomposition/formation reactions. Cyclic species are possibly involved in the formation mechanism of pyrocarbon.

1. INTRODUCTION

The use of pyrocarbon, i.e. of carbon deposited by pyrolysis of gaseous hydrocarbons, as a matrix in thermostructural composites aims to obtain pronounced refractory character, mass gain relatively to other families of composites and high performance mechanical properties [1]. Improvement of the mechanical properties of the composites in general can also be achieved by depositing a thin film of pyrocarbon as *interphase* between the matrix and the reinforcement. In this way, aromatic layers more or less parallel to the surface of the reinforcement are obtained [2]. During mechanical stressing of the composites the weak Van der Waals interlayer bonds yield first and permit limited debonding and fiber pullout.

When pyrocarbon is used as a matrix material, the yield of the deposition relatively to by-products like coke and soot and the decrease of the infiltration time and temperature are the important features in the deposition process. When it is used as interphase material, the morphology of the deposit, i.e. the extend and the orientation of the aromatic layers relatively to the reinforcement is the important feature. All these variables are function of the operating conditions through the composition of the gas phase in the vicinity of the deposition area. The knowledge of this reactive gas phase allows for the comprehension of the reaction mechanisms and consequently, for the optimization of both processes. It is the link between the overall operating parameters, which are accessible by the experimentalist and the characteristics of the obtained films.

In that which follows, a mass spectrometric study of the gas phase during the CVD of pyrocarbon will be presented, by sequentially processing the pyrolysis of pure methane CH_4 , of propane C_3H_8 , and of a mixture 80% CH_4 - 20% C_3H_8 , as a function of temperature and of surface-to-volume (S/V) ratio of the substrate. The composition of the gas phase is identified in each case. Reaction mechanisms are proposed for the homogeneous and the heterogeneous decomposition of the reactants.

2. EXPERIMENTAL

Experiments were conducted in a standard horizontal, hot wall quartz reactor of ~200 mm isothermal zone in the investigated conditions. Working pressure and gas flows were regulated by Baratron-gauge-monitored throttle valve and by PC-monitored mass flow meters respectively. Experiments were processed

by using Prodair Instrument Quality CH_4 and C_3H_8 and Prodair 5N helium, He, as a dilution gas. Deposition was performed on silicon nitride Si_3N_4 , polished flat substrates and on carbon fibers preforms.

Table 1: The investigated operating conditions for the decomposition chemistry of methane and/or of propane

Temperature, T	753-1293K (480-1020 °C)
Pressure, P	1333-2066 Pa (10-15.5 torr)
CH_4 flow	72-90 sccm
C_3H_8 flow	0-18 sccm
He flow	0-72 sccm
Total flow	29-388 sccm
C_3H_8 in the reacting gas phase	0-20 at%

Heating of the reactor was performed under 30 sccm of He. Sampling and analysis of the gases was initiated after an approximately 60 min stabilization period, corresponding to the regulation of flow in the mass spectrometer.

A PC-monitored Balzers QMH 420 quadrupole was connected to the reaction chamber through a micrometric valve and a 2 mm diameter quartz tube. At 953K (680 °C), i.e. just below the decomposition temperature of C_3H_8 in the adopted operating conditions, no change of the relative intensities of the ionic fragments was observed when quartz tubes with different lengths were placed within the isothermal zone of the reactor. It was thus checked that the sampling disposal does not originate heterogeneous reactions which could mask homogeneous gas phase reactions. During the experiments sampling was realized at the middle of the isothermal zone of the reactor.

The mass spectra of CH_4 and of C_3H_8 below their decomposition temperatures were initially recorded. They are in agreement with literature information [3], and help to establish in each case the reference state for the comparison with the spectra originated from the reaction products. These *baseline spectra* correspond to the fragmentation of the molecules originated from the electron bombardment in the ionization chamber at the entrance of the quadrupole. The decomposition rate of different ionic fragments is, in this way, calculated by using the relation:

$$T_D (\%) = (1 - I_x/I_0) * 100 \quad (1)$$

where I_0 represents the intensity of an ionic fragment characteristic of a gaseous species before decomposition and I_x represents the intensity of the same fragment at different stages of the decomposition process. The formation rate of an ionic fragment is calculated in a similar way, by using the relation:

$$T_f (\%) = (I_x/I_{\max}) * 100 \quad (2)$$

where $I_{\max}$ is the maximum intensity of the ionic fragment, generally obtained in conditions of total decomposition of the initial species. Above the decomposition temperature of the reactants the variations of these rates are characteristic of the evolution of the gas phase with temperature.

The ionic fragments which were selected as representatives of the studied species are presented in Table 2. Since it was not possible in this study to differentiate acetylene from ethylene, fragment 26 was taken as representative of both $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$. The intensity of each selected ionic fragment was systematically corrected relatively to contributions which were attributed to other species.

It is worth noting that it is difficult to perform a rigorous quantification of the composition of the reactants by using this technique, because the response of a species in the quadrupole depends not only on its ionization yield, but also on its diffusion coefficient in the gas phase

Because of the need to study the role of minor species in the gas phase chemistry during the pyrolysis, preliminary experiments were necessary for the determination of the imprecision of each measurement as a function of the relative intensity. From the obtained results it appears that variations of the intensities in the order of 10^{-13} or less are not significant, i.e. they do not allow for the unambiguous determination of the presence or not of the species in the spectrometer.

Table 2: Ionic fragments, selected as representatives of the studied species.

Species	H ₂	CH ₄	C ₂ H ₂ /C ₂ H ₄	C ₂ H ₆	C ₃ H ₄	C ₃ H ₆	C ₃ H ₈	C ₄ H ₆
Ionic fragments	2	16	26	30	19	41	43	54
Species	C ₄ H ₈	C ₄ H ₁₀	C ₆ H ₆	C ₆ H ₁₀	C ₆ H ₁₄	C ₇ H ₈	C ₇ H ₁₄	C ₈ H ₁₀
Ionic fragments	56	58	78	67	71	91	83	106

3. RESULTS AND DISCUSSION

3.1 Comparative study of the gas phase compositions during the pyrolysis of pure CH₄, of C₃H₈ and of a 20C₃H₈/80CH₄ mixture.

It was first verified that pyrolysis of CH₄ in typical chemical vapor infiltration (CVI) operating pressure, i.e. 2066 Pa (15.5 torr), is initiated near 1273K (1000 °C), in agreement with previous reports ([4] and references therein) and that hydrogen H₂, is the main gaseous by-product of the pyrolysis [5]. The same study was conducted for C₃H₈, (diluted in 80 at% He because of the elevated reactivity of pure C₃H₈ in the conditions of Table 1), with total gas flow = 90 sccm. As was previously shown ([6-8] and references therein), H₂, CH₄, C₂H₂/C₂H₄ and C₃H₆ are the main by-products of the pyrolysis of C₃H₈. These preliminary experiments illustrated the dominant reactions for the two processes, i.e. reaction (3) for CH₄ [5] and reactions (4) and (5) for C₃H₈ [7,9].

In view of the higher energy of C-H than C-C bonds in the C₃H₈ molecule (422 versus 352 kJ/mol), reaction (4) seems predominant over reaction (5). However it is worth noting that in the overall reaction mechanism for the pyrolysis of C₃H₈, secondary reactions leading to heavier linear and cyclic hydrocarbons become progressively predominant[10].

In order to evidence the influence of CH₄ on the decomposition mechanism of C₃H₈ a comparative study of the formation/decomposition rates of the ionic fragments was conducted, in the systems (20C₃H₈/80He) and (20C₃H₈/80CH₄) at 1293K (1023 °C). At this temperature the major part of CH₄ is still unaffected and, consequently, its contribution to the decomposition of C₃H₈ can be checked. Although CH₃[•] and H[•] radicals can also participate in the reactions, the evolution of H[•] was not considered since it can be originated from the decomposition of both CH₄ and C₃H₈.

The intensities of the ionic fragments characteristics of butadiene C₄H₆, butene C₄H₈, butane C₄H₁₀, cyclohexene C₆H₁₀, and xylene C₈H₁₀ are identical in both systems, indicating that CH₄ does not participate in the formation/decomposition reactions of these species. On the other hand the intensities of ionic fragments characteristics of H₂, ethane C₂H₆, propylene C₃H₆, benzene C₆H₆ and toluene, C₇H₈ increase when He is substituted by CH₄ while the intensity of the ionic fragment corresponding to acetylene/ethylene, C₂H₂/C₂H₄ decreases. These variations are presented in Table 3 and they are further illustrated in Figure 1 for the case of C₂H₆ by varying the percentage of CH₄ in the reactive gas phase.

C₂H₆ is formed following reaction (6) [3,4,11,12] and (7) [4]:

The production of C₃H₆ after reaction (5) and the excess of CH₄ seem to favor the left-to-right direction of reaction (8) reported in [4]:

However, the increase of C_2H_6 as evidenced in Figure 1 and the decrease of C_2H_4 (which can also be explained by the right-to-left direction of reaction (4) in the presence of CH_4), indicate that the opposite direction is preferred.

Table 3: Relative intensity of ionic fragments 2, 26, 30, 41, 78 and 91 resulting from the pyrolysis of (20 C_3H_8 /80 He) and (80 C_3H_8 /20 CH_4) mixtures and comparative variation (%). T = 1293K (1020 °C), P = 2066 Pa (15.5 torr).

Ionic fragment	Relative intensity		Variation $\Delta x/x$ (%)
	C_3H_8/He	C_3H_8/CH_4	
2 (H_2)	$2,7 \cdot 10^{-8} \pm 0,2 \cdot 10^{-8}$	$3,7 \cdot 10^{-8} \pm 0,2 \cdot 10^{-8}$	+37
26 (C_2H_2/C_2H_4)	$2,4 \cdot 10^{-8} \pm 0,2 \cdot 10^{-8}$	$1,6 \cdot 10^{-8} \pm 0,2 \cdot 10^{-8}$	-65
30 (C_2H_6)	$5,4 \cdot 10^{-11} \pm 0,5 \cdot 10^{-11}$	$1,3 \cdot 10^{-10} \pm 0,2 \cdot 10^{-10}$	+76
41 (C_3H_6)	$2,9 \cdot 10^{-10} \pm 0,2 \cdot 10^{-10}$	$5,6 \cdot 10^{-10} \pm 0,6 \cdot 10^{-10}$	+93
78 (C_6H_6)	$3,5 \cdot 10^{-9} \pm 0,2 \cdot 10^{-9}$	$4,2 \cdot 10^{-9} \pm 0,4 \cdot 10^{-9}$	+20
91 (C_7H_8)	$2,0 \cdot 10^{-10} \pm 0,1 \cdot 10^{-10}$	$3,3 \cdot 10^{-10} \pm 0,2 \cdot 10^{-10}$	+65

Figure 1: Variation of the decomposition rate of the ionic fragment 30, characteristic of C_2H_6 as a function of temperature for different compositions of a C_3H_8/CH_4 reactive gas phase. P = 2066 Pa (15.5 torr).

3.2 Influence of temperature on the gas phase composition

The influence of temperature on the composition of the gas phase was evidenced on the (20 C_3H_8 /80 CH_4) mixture at P = 2066 Pa (15.5 torr), by studying the evolution of the relative intensities of fragment 43 corresponding to C_3H_8 , of the fragments 2, 16, 26 and 41 corresponding to the major linear species, of the fragments 54 and 56 corresponding to heavy linear hydrocarbons and of the fragments 67, 78, 91 and 106 corresponding to cyclic hydrocarbons.

C_3H_8 is stable at low temperatures. It starts decreasing at 953K (680 °C) and it attains 0% at approximately 1180K (910 °C), corresponding to its total decomposition.

The major species of the reactive gas phase are H_2 , CH_4 , C_2H_2/C_2H_4 and C_3H_6 , in agreement with the results on the decomposition of C_3H_8 . Their evolution with temperature is presented in Figure 2. C_6H_6 , whose behavior will be discussed later, is also considered as a major species above 1173K (900 °C).

The increase of H_2 above 953K (680 °C) is principally due to the decomposition of C_3H_8 . The moderate increase at this temperature of CH_4 can be attributed to the decomposition of other hydrocarbons following the principle of reaction (4) and/or to recombinations like the one of reaction (9) [13]:

The decrease of CH_4 above 1223K (950 °C) is probably due to its direct decomposition. The comparison of this temperature with the temperature of 1273K (1000 °C) at which the decomposition of pure CH_4 is initiated, illustrates the influence of C_3H_8 on the decomposition of CH_4 . C_2H_2/C_2H_4 are absent below 993K (720 °C). Above this temperature they rapidly increase and they are roughly stabilized above 1213K (940 °C). These species are essentially originated from the direct decomposition of C_3H_8 .

The evolution of the so called heavy linear hydrocarbons C_4H_6 and of C_4H_8 , is presented in Figure 3. The formation of C_4H_6 above 988K (715 °C) is related to the formation of C_4H_8 . C_4H_8 is formed above 953K (680°C), which is the starting temperature for the decomposition of C_3H_8 following reactions (10) [14], or (11) [11,14]:

Figure 2: Pyrolysis of a mixture 20 C_3H_8 /80 CH_4 . Variation of the formation and of the decomposition rates of ionic fragments corresponding to species H_2 , CH_4 , C_2H_2/C_2H_4 and C_3H_6 as a function of temperature.

C_4H_6 is formed from the direct decomposition of C_4H_8 [15]. In addition to this on line process, other recombination reactions (direct or among radicals) have been proposed for the formation/decomposition of these species [15]. These reactions can explain the decrease of the intensity of fragment 56 at 1083K (810

°C) corresponding to the direct decomposition of C_4H_8 , the decrease of the intensity of fragment 54 at 1183K (910 °C) corresponding to the formation of $C_xH_3^+$ radicals with $1 \leq x \leq 3$, or the further increase of fragment 56 above 1243K (970 °C).

Figure 3: Pyrolysis of a mixture $20C_3H_8/80CH_4$. Variation of the formation and of the decomposition rates of ionic fragments corresponding to species C_4H_6 and C_4H_8 as a function of temperature.

The evolution of the cyclic hydrocarbons with temperature is presented in Figure 4. The general mechanism for the formation of cyclic species is initiated with C_4H_6 . C_4H_6 reacts with C_2H_4 to form C_6H_{10} [8,16] and finally C_6H_6 . Indeed, C_6H_{10} strongly increases above 993K (720 °C), which is also the formation temperature of C_4H_6 and of C_2H_4 . C_4H_6 also reacts with C_3H_6 to finally form C_7H_8 [15,16] and possibly with C_4H_8 to form C_8H_{10} .

3.3 Influence of the surface/volume (S/V) ratio on the gas phase composition

The influence of the surface/volume (S/V) ratio of the reactor on the composition of the gas phase was performed on the $(20C_3H_8/80CH_4)$ mixture at $T = 1293K$ (1020 °C) and $P = 2066$ Pa (15.5 torr). Experiments were conducted successively without substrate and with an increasing number of preforms. S/V was in this way varied between 0.9 and 35 cm^{-1} . It appears that when S/V increases the intensities of the fragments which are characteristics of the linear hydrocarbons remain unchanged. On the contrary, as shown in Figure 5, the intensities corresponding to the aromatic species C_6H_6 , C_7H_8 and C_8H_{10} decrease and that of H_2 increases. This behavior indicates that homogeneous and heterogeneous reactions coexist during the pyrolysis of hydrocarbons. It also seems to confirm that in the investigated conditions it is the aromatic hydrocarbons which participate in the heterogeneous reactions while the other species are mainly implied in the homogeneous reactions. It thus appears that the aromatic hydrocarbons are decomposed by a dehydrogenation process probably leading to the formation of pyrocarbon.

Figure 4: Pyrolysis of a mixture $20C_3H_8/80CH_4$. Variation of the formation and of the decomposition rates of ionic fragments corresponding to species C_6H_{10} , C_6H_6 , C_7H_8 and C_8H_{10} as a function of temperature.

Figure 5: Pyrolysis of a mixture $20C_3H_8/80CH_4$. Variation of the formation and of the decomposition rates of ionic fragments corresponding to species H_2 , C_8H_{10} , C_6H_6 and C_7H_8 as a function of the surface-to-volume ratio of the substrate.

4. CONCLUSIONS

The pyrolysis of CH_4 , of C_3H_8 and of the mixture $20\text{C}_3\text{H}_8/80\text{CH}_4$ was investigated in a hot wall CVD reactor by mass spectrometry. Experiments were conducted as a function of operating temperature and of surface-to-volume (S/V) ratio of the substrate. The main by-products of the pyrolysis of the mixture were identified as being: H_2 , CH_4 , $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$, C_3H_6 , C_2H_6 , C_4H_6 , C_4H_8 , C_6H_6 , cyclohexene C_6H_{10} , toluene C_7H_8 and dimethylbenzene C_8H_{10} . Based on the obtained results, reaction mechanisms were proposed taking into account homogenous decomposition/formation reactions. The variation of the S/V ratio helped to distinguish between heterogeneous and homogeneous reactions, evidenced the implication of the cyclic species in the heterogeneous reactions and showed that their decomposition is due to a dehydrogenation process, probably leading to the formation of pyrocarbon.

The correlation of these results with the characteristics of the obtained films, i.e. their growth rate and/or their morphology, is expected to establish the link between the overall operating parameters, which are accessible by the experimentalist and the aimed properties of the pyrocarbon.

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