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Residence time effect on fullerene yield in butadiene-based laser pyrolysis flame

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Abstract

A new route for fullerene synthesis by CO_2 -laser pyrolysis of gas phase mixture is proposed. Small hydrocarbon molecules which absorb the laser radiation, such as butadiene, are mixed with nitrous oxide (N₂O) as oxidizer. Such a mixture allows avoiding the use of a photosensitizer as SF₆ which causes contamination of the reaction zone and possibly influences the growth of fullerenic structures. This Letter also confirms the strong influence of the C/O atomic ratio in the mixture on the fullerene yield, and shows that residence time of the reactants in the pyrolysis flame and pressure influence dramatically the fullerene formation.

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1. Introduction

Since their discovery in carbon cluster beams [1], fullerenes have attracted much attention because of their potential use in medical, storage or electronic applications. An efficient synthesis method is still an important objective. Fullerenes are mainly produced by graphite vaporization [2] or from sooting flame [3–5]. Formation of fullerenes was also demonstrated by CO_2 -laser pyrolysis [6] and synthesis of macroscopic quantities

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was reported [7]. In particular, laser pyrolysis appears efficient for the production of higher fullerenes, which could be even more attractive for applications.

Laser pyrolysis is a flow method allowing the formation of nanopowders by homogeneous nucleation and growth in a reaction flame [8]. This method differs from combustion by the heat supply to the reactants: a continuous energetic transfer is ensured by the resonance between the laser radiation and the infrared absorption band of one of the precursors. In the case of fullerene production, the precursor mixture usually contains a photosensitizer which acts as a heat transfer agent due to the limited absorption of carbon precursors. Sulphur hexafluoride (SF₆) absorbs strongly the CO₂-laser radiation and was used as transfer

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agent. Although SF_6 is characterized by a high thermal and chemical stability, it was found to be not chemically inert in the specific conditions of laser pyrolysis [9], and could form radicals influencing the reaction pattern [10].

In this Letter, fullerenes are synthesized by laser pyrolysis of a hydrocarbon/oxidizer mixture without SF_6 . The objective is to study the fullerene formation as a function of the main synthesis parameters. In a previous Letter [11], the C/O atomic ratio in the precursor mixture was shown to influence strongly the fullerene yield. The highest yields were obtained for a C/O ratio close to 1.2, as in combustion experiments. Also, the C_{60}/C_{70} ratio was found to increase significantly for C/O ratio decreasing down to 1.2. These effects have been tentatively explained by a kinetic model [12] based on a molecular growth process where the C/O ratio is expected to influence the concentration of the radicals involved in the edification of closed-cage structures. This explanation will be checked here, including C/O value under 1.2, to verify the agreement with combustion data.

According to this explanation, residence time in the flame is a sensitive parameter which could lead to appreciable variations of higher fullerenes yield (beyond C_{70}). This parameter is valuable to study both heterogeneous and homogeneous nucleation [13]. In connection with the time required for fullerene formation, it could be modulated experimentally to increase the fullerene yield and particularly higher fullerenes. In this Letter, this effect was studied by means of total flow rate variation. The pressure is also a crucial parameter. Fullerenes appear in a bellshaped window of thermodynamic stability, limited by polycyclic aromatic hydrocarbons (PAH) at low temperatures (<1500 K) and mainly by acetylene (C_2H_2) at high temperatures (>2500 K). The pressure reduction enlarges this stability area and improves the conversion rates [14,15]. Laser pyrolysis performed at lower pressures could lead to larger fullerene yields, too. Pressure effects will be discussed in relation with residence time effects. Results obtained either by total flow or pressure variations will be compared to distinguish the respective influence of these parameters.

2. Experimental

The experimental set-up has been described elsewhere [11]. The CO₂-laser beam is focused by a ZnSe lens at its intersection with the reactant flow where power density up to 2.10^5 W/cm² are reached. Reactant gases are introduced through a 4 mm diameter nozzle and are mass-flow controlled. The pressure is kept constant by a downstream control system. The temperature is monitored with a monochromatic pyrometer. The reactant flow was a hydrocarbon/oxidizer mixture. Butadiene (C_4H_6) was chosen as carbon source, since it absorbs efficiently the 10P26 laser line at 938.69 cm⁻¹, due to its CH_2 wag mode at 907.8 cm^{-1} [16], and led to a reaction flame under oxidizing environment. N₂O has been maintained as oxidizing agent, since it gives better fullerene production than molecular oxygen [9,17].

The effect of three parameters was studied: residence time τ , work pressure P, and C/O ratio (Table 1). In the C253–C256 experiments, τ was varied by changing the total reactant flow without changing the other parameters (P = 400 Torr, $T \sim 1580$ K). The C/O ratio was fixed to 1.2 since this value appeared optimal previously [11]. To evaluate τ , the volume V of the reaction hot zone was appreciated with the optical pyrometer, as the flame volume having uniform brightness and so, almost uniform temperature. The expression for τ is

$$\tau = \frac{V}{D_0} \frac{T_0}{T} \frac{P}{P_0},\tag{1}$$

where D_0 is the total flow delivered by the mass flow-meters at standard pressure and temperature. A strong correlation between V and D_0 was observed (with a quadratic-like behaviour), by extension of the hot zone along the direction of the reactant flow. Calculation of τ accounts for these variations. V was the largest for the largest flow (C253). For higher flow, strong flame instabilities were observed. Then, it was not possible by flow variation to reduce τ below 7 ms. Contrary to the case of the photosensitised system [11], the flame temperature was not under laser power control but was mainly influenced by pressure and C/O ratio variations.

Table 1 Synthesis parameters for the samples obtained from C_4H_6/N_2O mixtures and yields determined by HPLC for $C_{60} + C_{70}$ and higher fullerenes

Sample	Studied parameter	Flow rate (cm ³ /min)		Velocity (cm/s)	C/O ratio	Т (К)	P (Torr)	τ (ms)	Soot (g/h)	C ₆₀ + C ₇₀ (%)			C ₆₀ /C ₇₀ ratio	C_{70+2n} (%) ^a in total fullerenes
		C_4H_6	N_2O							of total carbon	in soot	in total fullerenes		
C253	Residence	179	570	99	1.25	1583	400	7	1.2	0.04	0.8	88.2	1.3	6.9
C254	time τ	138	460	79	1.2	1573	400	7	0.5	0.06	2.1	88.7	1.5	6.8
C255		91	295	51	1.23	1588	400	8	0.2	0.01	0.2	86.4	1	3.1
C256		55	188	32	1.17	1578	400	11	0.5	< 0.01	0.03	99.9	0.8	_
C257	P at	89	289	50	1.23	1573	280	5	0.7	0.04	0.7	88.3	0.7	6.5
C258	fixed τ	179	588	101	1.22	1603	550	9	0.8	0.02	0.6	89.9	1.3	4.6
C259	P at	138	470	81	1.17	1388	280	3	0.3	0.07	4.4	92.1	2.1	3.6
C260	fixed flow	138	470	81	1.17	1618	550	11	0.7	0.03	0.7	89.7	1.3	4.3
C261	C/O ratio	110	487	79	0.9	1378	400	3	0.2	0.03	2.1	92.9	1.6	3.3
C262	(with C254)	165	425	78	1.55	1663	400	7	3	< 0.01	0.01	58.6	0.6	16.4

^a The sum of the $C_{70} + C_{60}$ and C_{70+2n} percentages is not equal to 100 due to the presence of extra peaks attributed to fullerene-oxide structures.

The aim of the C257–C260 experiments was to check the pressure influence by comparison with C254. In the first set (C257, C258), *P* was changed trying to keep τ constant by flow adjustment, while in C259 and C260 only *P* was varied, resulting in τ variations. Unfortunately, the temperature could not be maintained constant. Finally, the experiments C261–C262 had the goal to check C/O ratio effects.

Fullerenes were extracted from soot with toluene by the Soxhlet continuous extraction procedure. Separation and quantification of C₆₀, C₇₀ and higher fullerenes were performed by High Performance Liquid Chromatography (HPLC). Calibration of C₆₀ and C₇₀ contributions was made with solutions of known concentration of pure fullerenes. The three-dimensional analysis of the chromatograms (wavelength, elution time and absorbency) was obtained by a UV-Visible diode array detector, coupled with HPLC. This allowed the identification and comparison of the respective amount of the larger fullerenes (above C_{70}) in the soot through their normalised absorbency spectra in the UV-Visible range and areas of elution peaks normalised to the same mass (1 g) of soot. Extracted samples were analysed by Fourier Transform Infra-Red (FTIR) spectrometry.

3. Results and discussion

The data obtained from HPLC measurements (Table 1) show firstly that fullerenes are present in soot produced by laser pyrolysis of butadienebased mixtures. According to the experimental conditions, the $C_{60} + C_{70}$ yield varies from 58.6% to 99.9% of the total fullerene yield. Higher fullerenes (beyond C_{70}) are also observed, up to 16.45%. Signatures attributed to fullerene-oxide adducts were also detected on chromatograms. The best $C_{60} + C_{70}$ yield (0.06% of total consumed carbon) is obtained with a residence time around 7 ms (C254) at $T \sim 1600$ K, P = 400 Torr and C/O = 1.2. For the $C_6H_6/N_2O/SF_6$ system [11], higher values (up to 0.23%) were obtained in similar conditions but with a lower residence time (1 ms). It is a first indication that residence time is a determinant parameter.

3.1. Effect of the C/O ratio

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The results obtained from increasing C/O ratio (runs C261, C254 and C262, Table 1 and Fig. 1) confirm that this ratio has a strong effect on the fullerene formation and that C/O = 1.2 seems actually an optimum value. When C/O is reduced down to 0.9 (run C261), similar fullerene weight in soot (2.1%) is obtained than for C/O = 1.2 (run C254), but the soot efficiency is smaller (0.2 versus 0.5 g/h) and the C₆₀ + C₇₀ mass yield as well. In Fig. 1, the results obtained with the C₆H₆/N₂O/SF₆ system [11] are also reported. For C/O = 1.2, both fullerene weight in soot and C₆₀/C₇₀ ratio are similar, which suggests a negligible participation of

Fig. 1. Comparison of the effect of C/O ratio between laser pyrolysis and combustion (from Richter et al. [5]). (a) Fullerene $(C_{60} + C_{70})$ yield in soot and (b) C_{60}/C_{70} ratio. Open triangles are for combustion results, open diamonds for benzene-based mixtures for laser pyrolysis [11] and filled squares for present results (laser pyrolysis of butadiene-based mixtures).



radicals coming from SF_6 dissociation on fullerene growth. Values recorded by Richter et al. [5] for combustion flames are also reported for comparison in Fig. 1. The good agreement of the pyrolysis results with combustion data is confirmed.

The typical features of C₆₀ (527, 577, 1183, 1428 cm⁻¹) and C₇₀ (535, 565, 578, 641, 674, 795, 1134, 1430 cm⁻¹) are identified in FTIR spectra of toluene extracts (Fig. 2). While for runs C254 and C261 these features are evident, the absorption bands assigned to PAH (aromatic C–H deformations in the 700–900 cm⁻¹ range and CC stretch mode at 1640 cm⁻¹) are more underlined for run C262 where the C/O value is the highest.

The present results are consistent with the kinetic interpretation suggested previously [11]. C/O variation changes the concentrations of radicals involved in the nucleation and growth of fullerenes (H, H₂, C₂H₂) leading to a modification of the growth kinetic in the flame. Nevertheless, both $C_{60} + C_{70}$ yield and C_{60}/C_{70} ratio seem to be more sensitive to C/O variation in the case of butadiene

pyrolysis compared to benzene-based mixture pyrolysis (Fig. 1). The C/O variation from 1.2 (C254) to 1.55 (C262) provokes a steeper decrease of $C_{60} + C_{70}$ weight in soot (2.1–0.01%) and the C_{60}/C_{70} ratio falls much more rapidly (1.5–0.6). This could be related to the higher H content in the butadiene case, and possibly reflects an influence of the C/O ratio through its effect on hydrogen concentration in the reaction volume.

3.2. Effect of the residence time

In the experiments C253–C256 (C/O~1.2), the flow rate decrease leads to a τ increase from 7 to 11 ms. Since the hydrocarbon flow is not constant, the analysis of fullerene production will be done only in term of fullerene weight in soot or toluene extract. The striking changes in the FTIR spectra (Fig. 3) show that τ influences strongly the fullerene formation. C₆₀ and C₇₀ yields are reported in Fig. 4a as a function of τ . The results display similarities with



Fig. 2. FTIR absorption spectra for three extract samples with C/O ratio of 1.55 (C262), 1.2 (C254) and 0.9 (C261). Vertical arrows on the bottom axis indicate the positions of IR bands for C_{60} (open triangle) and C_{70} (filled triangle), respectively.



Fig. 3. FTIR absorption spectra for four extract samples for increasing residence time (C253, C254, C255, C256) at C/O = 1.2. Vertical arrows on the bottom axis indicate the positions of IR bands for C₆₀ (open triangle) and C₇₀ (filled triangle), respectively.



Fig. 4. Effect of the residence time on fullerene yield. (a) C_{60} (open symbols) and C_{70} (filled symbols) yields from flow variations for increasing pressures: 280 Torr (circles), 400 Torr (triangles) and 550 Torr (diamonds); (b) ($C_{60} + C_{70}$) yield from pressure variations (filled diamonds) and flow variations (open squares).

the C/O effect. As τ increases, the yield decreases and the C₆₀/C₇₀ ratio also decreases. From the kinetic model [12], large residence times are more favourable to fullerene formation and particularly C₇₀. It is consistent with the present decrease of the C₆₀/C₇₀ ratio when τ increases, but the expected increase of the total yield is not observed. On the contrary, a strong decrease is observed by HPLC measurements and confirmed by the FTIR spectra (Fig. 3). This yield decrease is not well understood. An effect coming from oxidation of the closed cage structure could be invoked.

3.3. Effect of the pressure

C257–C260 runs were performed to evaluate the pressure influence (Table 1). In C257 and C258

runs, we have tried to keep τ constant by total flow adjustment. Unfortunately, as discussed above, the correlation between *P*, the hot zone volume *V* and τ , is such that τ changes each time *P* is changed. In C259 and C260 runs, *P* was changed but with constant total flow, thus τ variations are even more important. Fig. 4a reports the dependence of the C₆₀ and C₇₀ yields with variation of τ induced by flow variations at different pressures. The strongest yields are obtained for the lowest τ . However, at 550 Torr, the yields are quite constant between 9 and 11 ms but stronger than the yields at 400 Torr. This could be explained by a higher flame temperature at 550 Torr.

In Fig. 4b, one can see that the $C_{60} + C_{70}$ yield evolves differently with τ depending on whether τ is varied by changing the pressure (at constant reactant flow) or the reactant flow (at constant pressure). The yields obtained by pressure variation are higher than those obtained by flow variation. Lower τ are better for fullerene formation as well as low pressures. Unfortunately, it was not possible to investigate τ shorter than 7 ms by flow variation due to flame instabilities. The pressure reduction is more efficient to reduce τ down to 3 ms where the highest yield is observed. A similar increase of the fullerene yield was observed previously for benzene-based pyrolysis [11] when τ and T were reduced respectively to about 1 ms and 1650 K. This result was interpreted by an inhibiting effect of SF₆ at high temperature. The present results suggest that this inhibiting effect is weaker than supposed.

According to global equilibrium prediction for C_{60} and C_{70} [15], when *P* decreases, both threshold and maximum temperatures of the bell-shaped window of thermodynamic stability are shifted towards lower values. At the same time, there is an abrupt change (over a range less than 100 K) from PAH to fullerenes when temperature increases [15]. These thermodynamic considerations are in agreement with our results showing a large yield at low pressure for the lowest measured temperature (sample C259, Fig. 4b). In that case, $C_{60} + C_{70}$ represent 4.4% of the soot which is close to the maximum value reported in combustion experiments [5] at much lower pressures (around 50 Torr, see Fig. 1a). This value is higher than those obtained by laser pyrolysis of benzene-based mixtures [11].

Another interesting effect of the pressure reduction is that the C₆₀ yield exceeds the C₇₀ yield at a lower residence time (Fig. 4a). At 550 Torr, it is located beyond 12 ms while at 400 Torr, the value is close to 8 ms and near 4 ms at 280 Torr. Also, the C₆₀ yield variations with τ are more rapid at low pressure compared to C₇₀ yields. Therefore, the fullerene yield seems to be much more sensitive to residence time variations at low than at high pressure.

3.4. Higher fullerenes

The yield of the higher fullerenes (C_{74}, C_{76}, \ldots) is the largest (16.4%) for C262 run (Table 1), and goes with very low $C_{60} + C_{70}$ yields, suggesting quite different stability domains for higher fullerenes and $C_{60} + C_{70}$. This effect could be due to different C/O ratio (comparison of C254 and C262). The edification of large closed-cage needs the addition of large flat carbonaceous fragments to cage nuclei. When C/O is too low, these species are more oxidised and their proportion decreases. By contrast, low C/O values are favourable to radicals involved in the edification of C₆₀ and C₇₀ nuclei (carbon sheet including 5 member rings). Also, high C/O value leads to high soot efficiency (3 g/h), suggesting a prevalent heterogeneous growth mechanism. Soot particles could act as heat carriers that prolong the growing time and favour the higher fullerenes formation [18]. Thus, less oxidizing environments favour higher molecular weight. Flame temperature can also be invoked since the highest yield corresponds to the highest temperature. This parameter could be relevant for higher fullerene formation.

4. Conclusion

Experiments using butadiene-based mixtures for fullerene synthesis by laser driven-gas phase pyrolysis were successful. The study of the C/O ratio effect confirms previous results obtained in SF₆-photosensitised benzene-based mixtures, with an optimum value of C/O around 1.2 for C₆₀ and C₇₀ production. Thus, the role of SF₆ in this process is weaker than suggested previously. The yields (% of the soot) are constant through variation of C/O from 1.2 to 0.9 but the production is reduced due to a decrease of the soot production at C/O = 0.9. Then, the expected effect of the C/O ratio on kinetic growth is confirmed by study of the residence time which appears definitely as a very sensitive parameter for fullerene formation. The lowest residence times are more favourable to C_{60} and C_{70} formation as suggested in the benzenebased system study. Low pressures are also found to favour the C_{60} and C_{70} formation in agreement with thermodynamic predictions.

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