# LASER PYROLYSIS PRODUCTION OF NANOSCALE CARBON BLACK

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Key words: laser pyrolysis, carbon black, catalysis, fullerenes

## INTRODUCTION

Laser pyrolysis [1] is a versatile non-equilibrium thermodynamic process for the production of nanoscale particles involving fast growth, and rapid heating/cooling rates (~100, 000 °C/s) in the reaction zone defined by the intersection of a reactant gas stream and high power infrared ($CO_2$) laser. Using this technique, we have recently produced nearly pure phase nanocrystalline particles of $\alpha$-Fe, $Fe_3C$, and $Fe_7C_3$ [2]. This research, and our interest in fullerenes (e.g., $C_{60}$), motivated us to consider whether or not we could extend the laser pyrolysis technique to produce the other endpoint material, e.g., pure, or nearly pure nanocrystalline carbon, and perhaps fullerenes. $CO_2$ laser pyrolysis production of carbon soot from acetylene ($C_2H_2$) decomposition was reported by Maleissye et al. [3] and Yampolskii et al.[4]. They found reaction products are close to those obtained in a classic pyrolysis. In this paper, we report the results of a study involving catalytic decomposition of benzene ($C_6H_6$) to produce carbon black. Using small quantities of Fe as a catalyst, we obtained nearly pure carbon soot comprised of amorphous, spherical carbon particles with an average dia.~ 20 nm. These carbon nanoparticles appear to best resemble acetylene black, which identifies a nanoscale carbon soot prepared by the oxidation or thermal decomposition of acetylene [5]. We have furthermore subjected our nanoscale soot to a 2800 °C high temperature treatment (HTT) under Ar gas which promotes the transformation of the disordered spherical soot particles to particles of approximately the same size, but with polygonal facets and, in many cases, a hollow core. Pyrolytic carbon planes are observed aligned parallel to the facets on the heat treated particles, as seen in TEM lattice fringe images. We have no evidence, as yet, that fullerenes were produced along with the nanoscale soot.

To produce nanocrystalline $\alpha$-Fe and Fe-carbides, we have investigated recently the laser driven reaction of $Fe(CO)_5$ and ethylene ($C_2H_4$) following the process described in patents submitted by Exxon researchers [6, 7] who reported the production of $Fe_3C$ (cementite). To produce carbon black as an extension of this reaction, we first tried the obvious step, namely that of reducing the relative concentration of $Fe(CO)_5$ in the reactant gas stream. These experiments failed to produce significant amounts of carbon black, yielding instead nanoscale $Fe_7C_3$ with a thick coating of pyrolytic carbon. We next tried the addition of benzene ($C_6H_6$) to the reactant gas stream, and large amounts of fairly uniform size nanoscale carbon soot was thereby produced. Subsequent experiments revealed that this reaction requires the presence of only small amounts of

Fe(as a catalyst) to promote the formation of the carbon black. Carbon soot prepared in this way is the subject of this paper.

SYNTHESIS

Our laser pyrolysis system is shown schematically in Fig. 1, and is similar to that described by Haggerty [1]. The reactants ($Fe(CO)_5$, $C_2H_4$ (99.99%) and $C_6H_6$ (HPLC grade)) are introduced into the reactant gas stream by bubbling $C_2H_4$ through a solution of $C_6H_6$:$Fe(CO)_5$ = 50:1 (by volume) contained in a trap, as shown. The reactant gases then flow vertically out of a stainless steel nozzle inside the 6-way stainless steel cross (chamber) and intersect a horizontal beam from a $CO_2$ laser (Laser Photonics Model 150). The $C_2H_4$ flow rate was regulated to be ~100 sccm. Using ~15, 000W/mm$^2$ incident power density in the reaction zone, a bright white flame was observed. The energy coupling of the laser to the reactant gas is realized by tuning the laser frequency to the P20 line (945 cm$^{-1}$), which is shifted 5 cm$^{-1}$ relative to the strongest nearby rotational-vibrational absorption line of $C_2H_4$ at 950 cm$^{-1}$. A ZnSe lens was used to adjust the position of the $CO_2$ laser beam waist relative to the nozzle tip. If no $Fe(CO)_5$ is present in the stream, almost no soot is produced. From our previous work[2], if no benzene is present (only $C_2H_4$ and $Fe(CO)_5$), then Fe-carbides are formed. We therefore speculate that $Fe(CO)_5$ in the presence of both $C_2H_4$ and $C_6H_6$ acts as a catalyst, dehydrogenating the benzene and forcing the benzene molecule to fragment in the pyrolysis flame, leading to carbon soot formation. The chemical role of the $C_2H_4$ may not be important, other than to allow heat energy from the laser to be pumped into the reaction.

After leaving the pyrolysis zone, the particles, protected by a lamellar, co-axial flow of Ar gas, are collected in a Pyrex trap (Fig. 1). A teflon membrane filter (pore size 200 nm) was used to protect the mechanical pump. In the steady state, using a reactant gas nozzle with circular 5 mm dia. opening, a 4 - 6 mm diameter, well-collimated stream of particles can be seen to drift up the center of the 1 cm (I.D.) glass tube connecting the 6-way cross and Pyrex particle trap. A 0.5g/hour production rate of carbon black was obtained under the conditions described above. Mass flow controllers were used to control the supply of Ar (99.999%) to the coaxial sheath and to the cell windows; a separate controller was used to control the flow of the reactant gas mixture. Further details of our laser pyrolysis apparatus are available elsewhere [2].

RESULTS AND DISCUSSION

Subsequent to the synthesis, standard elemental analyses were applied to our carbon black samples for Fe, C, N, and H. The results of this analysis yield a composition $C_{10}Fe_{0.01}H_{1.2}N_{0.1}$. It should be noted that the C:H ratio is ~ 8, close to the ideal value ~10 predicted for acetylene black using a polycondensation model , and this value is lower than that obtained for a typical acetylene black, which has C:H ~40 [5]. The C:Fe ratio was also measured using electron microprobe analysis (EDX), resulting in C:Fe ~ 700, consistent with the value ~1000 obtained from the elemental analysis.

Shown in Fig. 2 are the high resolution TEM data taken using a JOEL 4000 electron microscope on "as synthesized"(2a, 2b) and heat treated (2800 °C in Ar) (2c, 2d) carbon blacks produced by laser pyrolysis. As shown in Fig. 2a, untreated carbon black particles present, on average, a well developed spherical shape, with an average particle diameter on the order of 20 nm. Typical of acetylene black, significant agglomeration was observed [5]. It is difficult to determine to what extent the particles might be fused, however. Fig. 2b is a magnified image within particle. Although the formation of very primitive carbon planes is observable in some regions of selected particles, most carbon black particles appear to exhibit an image of a highly disordered graphitic carbon (see the discussion of the x-ray results below).

Using the standard $N_2$ BET technique, we determined a value 50 $m^2/g$ surface area for the "as-synthesized" carbon black. This value is slightly lower than 70 $m^2/g$ reported for a typical acetylene black, and is lower than the theoretical surface total surface area for a 20 nm spherical particles (150 $m^2/g$). Consistent with this observation of a lower surface area, is that no significant cracking of the particle surface or accessible internal pores are apparent in the TEM photos (Fig. 2b) and that agglomeration (with possible fusion) of the particles is also observed.

Furthermore, the carbon black samples subjected to 2800 °C HTT in Ar show clear evidence for graphitization, consistent with lattice fringes from parallel carbon planes and the associated lattice plane spacing(Fig. 2d). As shown in Fig. 2c and 2d, heat treated particles, in many cases, exhibit parallel carbon layers in polygonal shapes about a hollow center. This suggests that crystallization is initiated at the particle surface. Finally, we did not observe any evidence for the presence of Fe or Fe carbides as small particles within the carbon black particle, or, in particular, at the particle core, or as a separate nanoparticle. This is consistent with the small amount of Fe observed in the carbon black (0.5wt %), suggesting that the Fe may be atomicly dispersed throughout the soot.

Shown in Fig. 3 are XRD results obtained with a Rigaku powder diffraction unit using Cu $K_\alpha$ radiation. Results for "as synthesized" (Fig. 3a) and low temperature HTT (900 °C in $N_2$) (Fig. 3b) carbon black samples are presented. The low HTT sample was produced with a higher than normal amount of $Fe(CO)_5$. As a result, this sample exhibited x-ray diffraction peaks associated with the existence of nanocrystalline $\alpha$–Fe and $\gamma$–Fe, as indicated. The diffraction peaks for the "as synthesized" sample are similar in width to that of a typical acetylene black [5]. Broad peaks are observed and indexed according to a convention for acetylene blacks based on graphite: in decreasing intensity, they are the 002, 10, and 11 diffraction lines, respectively. The average lattice constant along the c-axis, as determined from the 002 peak position, is found to be 3.65 Å, somewhat larger than normally observed (<3.5 Å) for acetylene black. A significant shift of 002 peak is observed after a 900 °C HTT in $N_2$ for 24 hrs(Fig. 3b), where again from the 002 peak, the lattice constant has decreased to 3.48 Å, closer to that of a typical acetylene black (3.43 Å).

Further work will be necessary to determine the role of Fe as a catalyst in the production of carbon black by the laser pyrolysis process.

ACKNOWLEDGEMENTS

This work was supported, in part, by the University of Kentucky Center for Applied Energy Research and the United States Department of Energy. We wish to thank Gerald Thomas and Mark Stewart for assistance in the characterization of the carbon black, and acknowledge helpful discussions with Frank Derbyshire.

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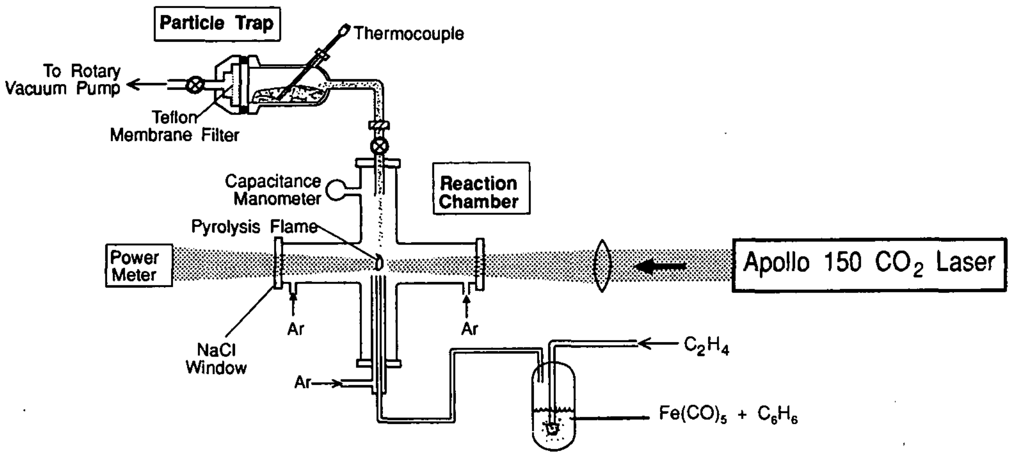


**Fig. 1 Laser pyrolysis system for the production of carbon blacks.**

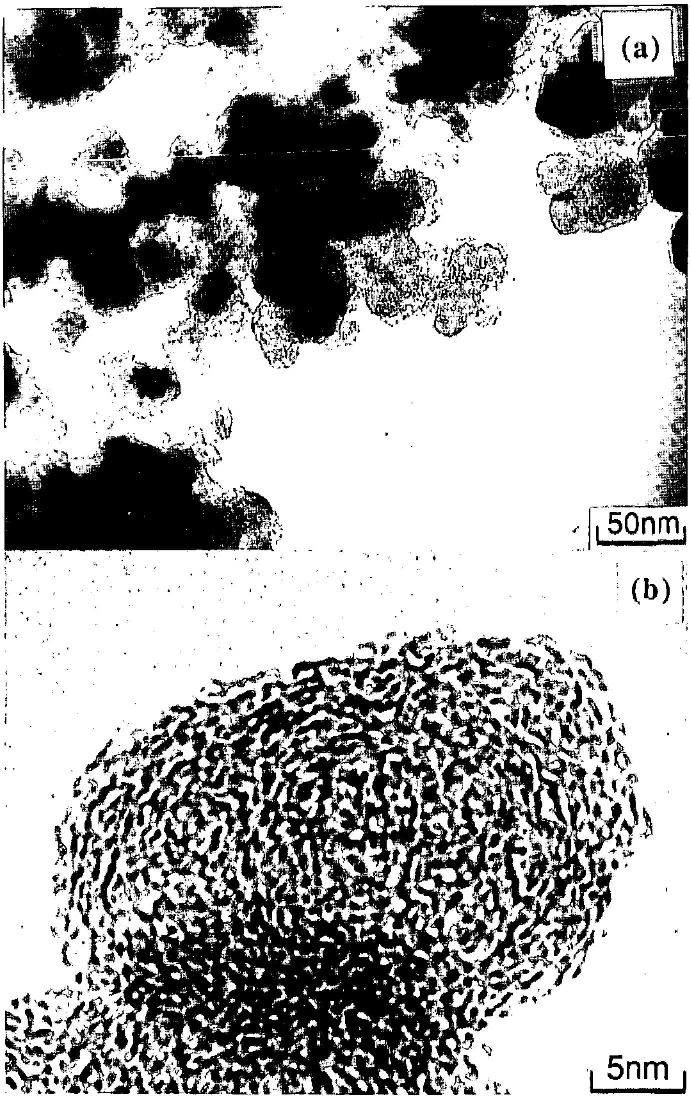


**Fig. 2a,b** TEM data for "as synthesized" carbon blacks produced by laser pyrolysis.

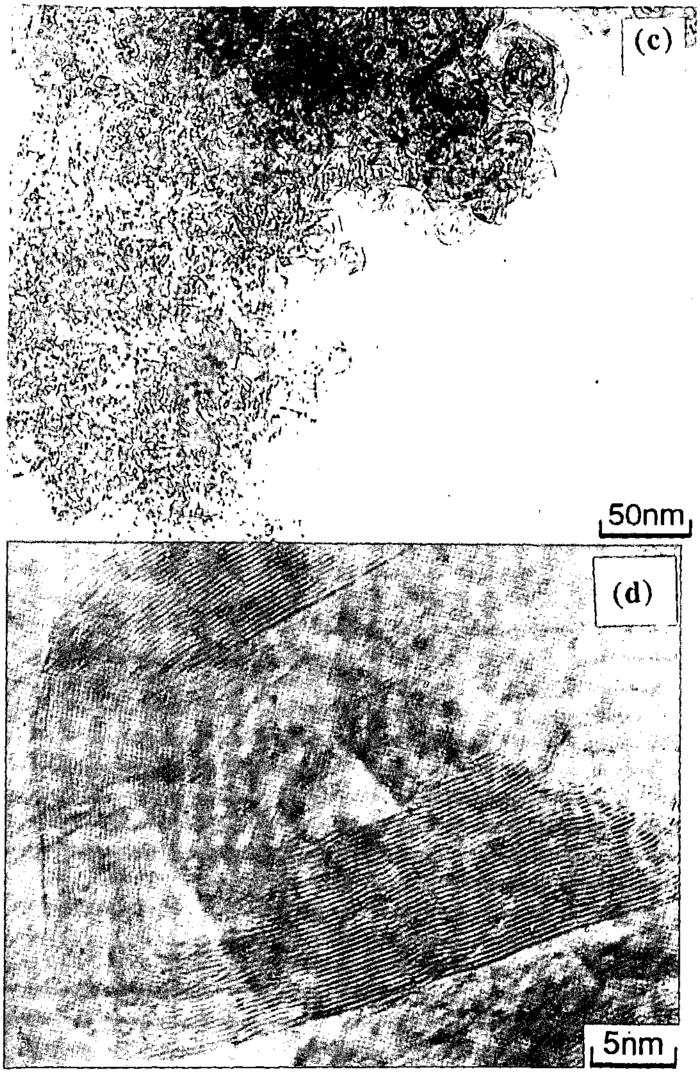


**Fig. 2c,d TEM data for heat treated (2800 °C in Ar) carbon blacks produced by laser pyrolysis.**

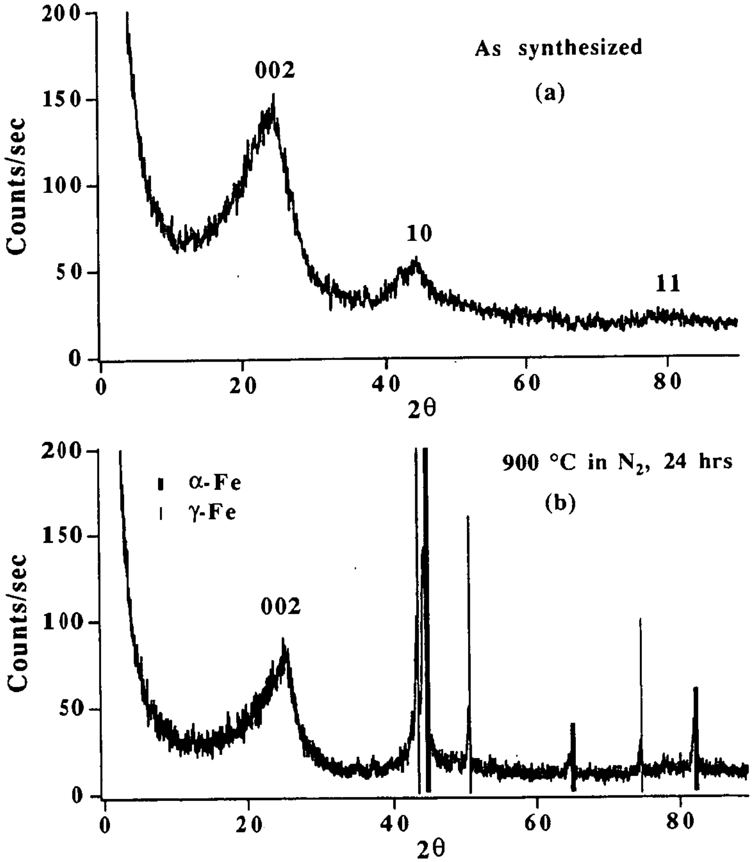


**Fig. 3** XRD(Cu Kα, λ=1.5418 Å) data for "as synthesized" (3a) and heat treated (900 °C in $N_2$) (3b) carbon black samples produced by laser pyrolysis. Vertical lines are obtained from standard powder diffraction data file.