

PRESSURE PYROLYSIS OF PYRENE UNDER NITROGEN AT MODERATE TEMPERATURES

Gilceia L. S. Vassem¹, Francisco G. Emmerich¹, Alfredo G. Cunha¹,
Jair C. C. Freitas¹, André A. de Souza² and Tito J. Bonagamba²

¹Laboratory of Carbon and Ceramic Materials, Department of Physics, Federal University of Espírito Santo, 29075-910, Vitoria-ES, Brazil

²Institute of Physics of São Carlos, University of São Paulo, P.O. Box 369, 13560-970, São Carlos-SP, Brazil

Introduction

The conversion of organic compounds to solid carbon materials is a complex process, which includes a variety of chemical reactions, involving many intermediate stages [1].

Greinke and Lewis [2] studied the carbonization of naphthalene, observing pitch, mesophase and coke formations, mainly through polymerizations with the loss of hydrogen. In spite of using a pure compound as a precursor, the residues of the pyrolysis were complex mixtures of compounds.

It is well known that the use of catalysts, as performed by Mochida et al. [3], allows the conversion of aromatic hydrocarbons into pitches and cokes using much lower temperatures than without a catalyst. Nonetheless, in this work we have studied the pyrolysis of a pure compound (pyrene) without the use of catalysts with the objective of better understanding the process of pitch formation, among other effects.

Experimental

Commercial pyrene (C₁₆H₁₀) with 98% of purity was used as the starting material. The heat treatments were performed under an inert atmosphere of nitrogen to a final pressure around 6.9 MPa in a laboratory-built vertical reactor. A constant heating rate of 10 °C/min was used and the final temperatures of treatment were 400, 450 and 500 °C, with residence times of 0, 1, 2, 4 and 8 h. A sample with a longer residence time of 16 h was also prepared at 500 °C. During the heat treatments the reactor was continuously agitated to improve the homogenization of the samples [4].

The produced heat treated samples were studied by using elemental analysis, TGA, XRD, solid-state ¹³C NMR and SEM. Instrument settings and sample preparation details are given elsewhere [5,6].

Results and Discussion

The heat treatments caused a segregation of the samples that increases progressively with the residence time at each final temperature. The heat treated samples were then separated into two well-defined regions (named A and B regions) with very different colors (region B is much darker than region A). The materials corresponding to regions A and B were collected from the top and the bottom of the reactor, respectively.

The results of elemental analysis and of other techniques indicated that the samples heat treated at 400 and 450 °C did not present significant changes as compared to the elemental composition of the precursor (C = 95.2 wt.% and H = 4.8 wt.%; atomic C/H = 1.65).

Table 1 gives the elemental composition of the samples treated at 500 °C. No significant changes were observed in the composition of the samples 500-0h to 500-4h, 500-8hA and 500-16hA as compared to the precursor. The atomic ratio C/H of the 500-8hB sample (2.05) is similar to that of a coal tar mesophase pitch (C/H = 2.08) [7] and larger than the mesophase pitches from naphthalene (C/H = 1.92) and dimethylnaphthalene (C/H = 1.86) [2]. On the other hand, the atomic ratio C/H of the sample 500-16hB (2.58) is of the order of usual cokes (C/H > 2.5) and larger than that of naphthalene coke (~ 2.21) [2] and dimethylnaphthalene coke (~ 2.23) [2].

Table 1. Elemental analysis of pyrene heat treated at 500 °C

Sample	C (wt %)	H (wt %)	C/H (atomic)
500-0h	95 (1)	4.9 (1)	1.62 (5)
500-1h	95.1 (9)	4.9 (1)	1.64 (4)
500-2h	95.1 (5)	4.9 (1)	1.62 (3)
500-4h	95.3 (1)	4.7 (1)	1.68 (1)
500-8hA	94.9 (9)	5.1 (1)	1.57 (4)
500-16hA	95 (1)	5.1(1)	1.57 (6)
500-8hB	96.1 (8)	3.9 (1)	2.05 (4)
500-16hB	96.9 (6)	3.1 (1)	2.58 (6)

Fig. 1 presents the XRD patterns of the samples treated at 500 °C. A significant broadening of all XRD peaks was observed from 4 h of heat treatment at 500 °C. A clear breakdown of the structure of the precursor (solid pyrene) was observed in the 500-8hB sample, where many peaks disappear and some remain broader, composing an enveloped broad line, which was more defined in the 500-16hB sample. This broad line of the 500-16hB sample corresponds to the (002) line of turbostratic carbon [8].

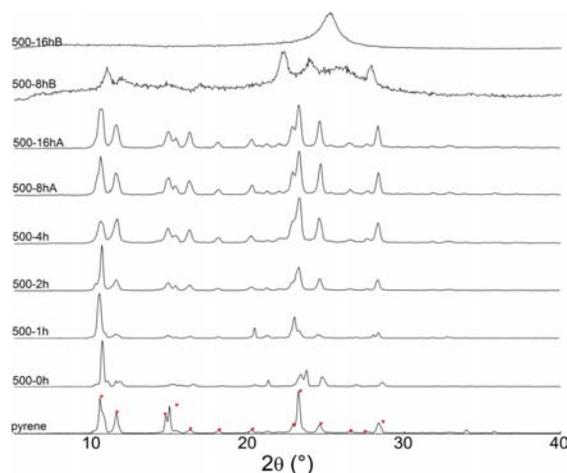


Fig. 1 XRD patterns of pure and heat treated pyrene samples under pressure at 500 °C.

The solid-state ^{13}C NMR spectra of the same series of samples are shown in Figure 2. The spectra corresponding to the samples with residence times up to 4 h and the spectra corresponding to samples 500-8hA and 500-16hA were all similar to the spectrum of the original compound, with two well-defined peaks in the aromatic region of ^{13}C isotropic chemical shifts [9]. On the other hand, the 500-8hB and 500-16hB samples exhibited spectra very different from the other ones, with the development of a broader single resonance centered close to 126 ppm. Such line is also in the region of the spectra associated with aromatic species, but the absence of the typical splitting observed for the pyrene molecule evidenced that starting from 8 h of residence time there was, at least in part of the material, a marked change in the initial molecular organization. The observed resonance is typical of disordered carbonaceous materials [9,10], with the formation of aromatic lamellae associated with the turbostratic structure, in agreement with the XRD patterns of these samples. The strong intensity observed in these spectra (recorded with ^1H - ^{13}C cross polarization) indicated that even in those two samples (with the largest C/H ratios in the series) there was a reasonable number of hydrogen atoms, probably at the edges of the aromatic lamellae, allowing an efficient transfer of polarization to ^{13}C nuclei through the ^1H - ^{13}C dipolar coupling.

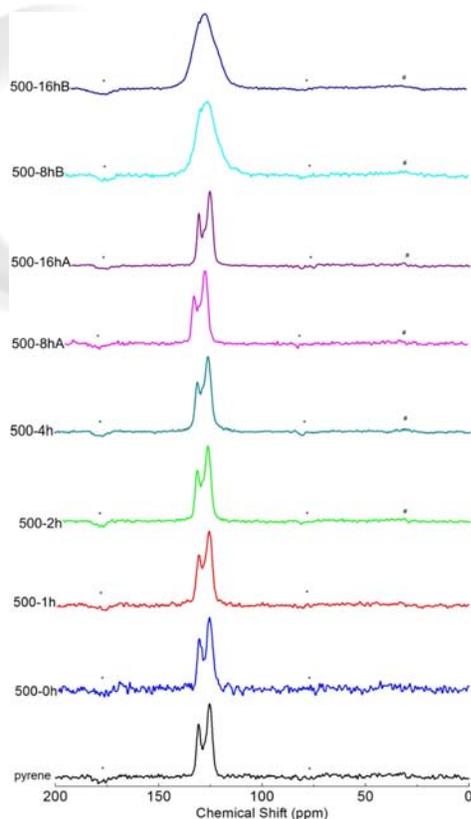


Fig. 2 Solid-state ^{13}C NMR spectra of pure and heat treated pyrene samples under pressure at 500 °C. Stars denote spinning sidebands.

Conclusions

The pyrene samples heat treated at 500 °C under pressure presented significant chemical, physical and structural changes starting from 8 h of residence time. The treatments with 8 and 16 h of residence time led to a clear segregation, with the material separated into two well-defined regions (A and B regions).

The 500-8hB sample presented the characteristics of an anisotropic carbon material; the results of elemental analysis and TGA [5,6] for this sample were similar to some mesophase pitches. On the other hand, the results of elemental analysis, XRD and SEM [5,6] indicated that the sample 500-16hB was similar to a coke.

The solid-state ^{13}C NMR spectra recorded for the 500-8hB and 500-16hB exhibited a single resonance associated with aromatic species. The absence of the splitting of the aromatic peak in these samples, which was typically observed for pure pyrene and for the samples with shorter residence times, evidenced the change of the initial molecular organization of the precursor, with the beginning of the formation of the aromatic lamellae associated with the turbostratic structure of disordered carbon materials.

Acknowledgments. The authors acknowledge the support from the Brazilian agencies CAPES, CNPq, FINEP, FAPESP and FAPES, and from ArcelorMittal.

References

- [1] Fitzer E, Muller K, Schafer W. The Chemistry of the pyrolytic conversion of organic compounds to carbon. In: Walker Jr PL, editor. Chemistry and physics of carbon, vol. 7. New York: Marcel Dekker; 1971. p. 237- 383.
- [2] Greinke RA, Lewis IC. Carbonization of dimethylnaphthalene and naphthalene. Carbon 1984;22(3):305-14.
- [3] Mochida I, Shimizu K, Korai Y, Otsuka H, Korai S. Structure and carbonization properties of pitches produced catalytically from aromatic hydrocarbons with HF/BF₃. Carbon 1988; 26(6):843-52.
- [4] Scaroni, AW, JeNkins RG, Walker Jr PL. Carbonization of anthracene in a batch reactor. Carbon 1991;29(7): 969-80.
- [5] Vassem GLS, Pirólise do pireno sob pressão com nitrogênio em temperaturas moderadas. Master in Science Dissertation, Post-Graduation Program in Physics, Federal University of Espírito Santo, Vitoria, Brazil, 2008:107p.
- [6] Vassem GLS et al. To be published (2010).
- [7] Andrésen J M, Zhang Yi, Burgess CE, Shobert HH. Syntesis of pitch materials from hydrogenation of anthracite. Fuel Processing Technology 2004;85:1361-72.
- [8] Emmerich FG. Evolution with heat treatment of crystallinity in carbons. Carbon 1995;12(33):1709-15.
- [9] Freitas JCC, Bonagamba TJ, Emmerich FG. ^{13}C high-resolution solid-state NMR study of peat carbonization. Energy Fuels 1999;11:53-59.
- [10] Freitas JCC, Bonagamba TJ, Emmerich FG. Investigation of biomass- and polymer- based carbon materials using ^{13}C high-resolution solid-state NMR. Carbon 2001;39:535-45.