

SYNTHESIS OF CARBON NANOSPHERES FROM PETROLEUM RESIDUES

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Introduction

A number of potential applications for carbon nanospheres have been identified, including catalyst support, lithium-ion battery electrodes, lubricants, field emission devices and biosensors. Carbon nanospheres have been produced successfully by chemical vapor deposition (CVD) from a variety of pure hydrocarbons, light hydrocarbon mixtures, and solid by-products of petroleum refining. Feedstocks from petroleum refining such as FCC bottom are a traditional raw material for the production of carbon materials but their use in CVD production of nanomaterials has not been properly studied.

Experimental

Heat treatment of decant oil samples for the production of petroleum pitches yielded, as a by-product, lighter residues suitable for vaporization [1]. Three such residues (Table 1), representative of the observed variation in physico-chemical properties, were fed into a vertical tube furnace at temperatures between 800 and 1200° C, at feed rates of 5 and 15 mL/h, without addition of catalyst. Argon and nitrogen were used as carrier gases at flow rates of 0,7 and 1,3 L/min.

Table 1. Properties of residues used as precursors

	A	B	C
Density (g/cm ³)	1,055	1,022	0,954
¹³ C NMR Aromaticity (%)	72,9	59,0	45,4
¹ H NMR Aromaticity (%)	34,4	25,0	15,3
% C	87,17	87,70	84,72
% H	7,53	8,55	9,71
% N	0,38	0,67	0,19
% S	0,81	0,66	ND
% O (diff)	4,11	2,42	5,38
C/H	0,972	0,861	0,732

Results and Discussion

Carbon nanospheres were obtained at temperatures of 1000° C and higher (Figure 1). Nanosphere purity depended on process temperature, with samples produced at 1000° C containing ~3-5% of organic byproducts, not observed in samples produced at 1200° C (Figure 2 e Figure 3). Spheres produced at 1200° C showed a higher oxidation resistance, with oxidation peak at 620-640° C, compared to 580-590° C for spheres produced at 1000° C but XRD analysis did not reveal

significant differences in structure between the samples, as the 002 peak is too wide for accurate determination of d_{002} and Lc.

Process temperature was identified as the most important variable. Besides higher product purity and oxidation resistance, higher temperatures favored higher yields and smaller diameters for all combination of other process variables.

Nanosphere diameters followed a lognormal distribution (Figure 4), typical of processes where the velocity of particle growth is proportional to its surface area and the residence time is distributed lognormally, due to simultaneous diffusion and drift [2], with most probable diameters ranging from varied from 100nm to 600nm.

Mass yields depended strongly on reaction conditions, especially temperature and flow rate of precursor, varying between 20 and 50%.

Similar results were obtained for the three different residues employed (Figure 5), showing that the process is fairly robust and adequate for large scale production, where variations in feed composition are to be expected.

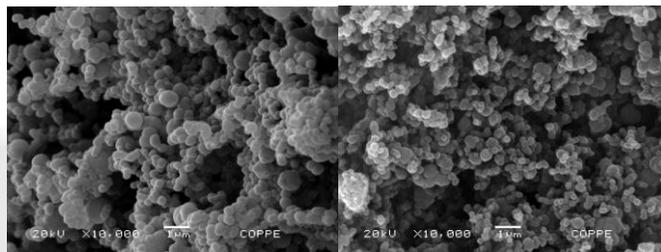


Fig. 1 SEM image of nanospheres produced at (a) 1000° C and (b) 1200° C

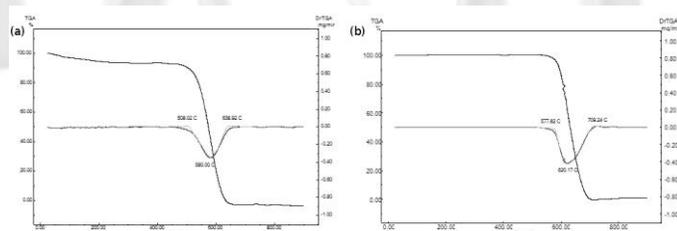


Fig. 2 TGA of nanospheres obtained at (a) 1000° C; (b) 1200° C.

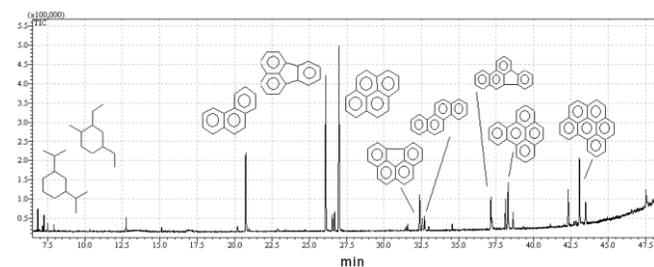


Fig. 3 GC-MS analysis of toluene extract of nanospheres produced at 1000° C.

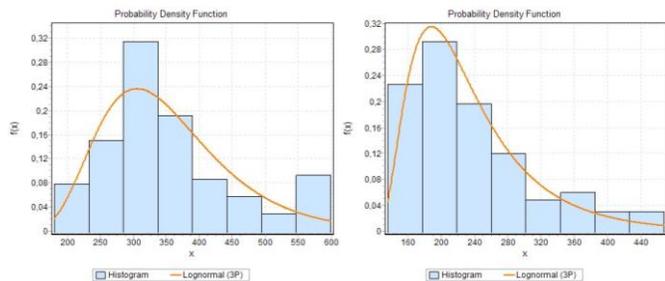


Fig. 4 Diameter distribution of spheres obtained in 1,3L/min argon, precursor feed rate of 15mL/h at (a) 1000°C (b) 1200°C

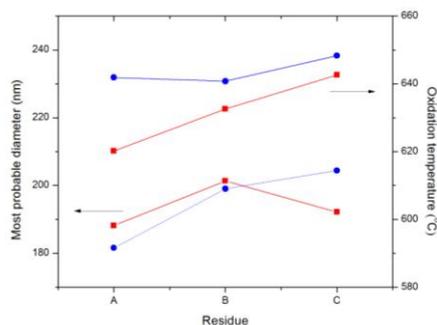


Fig. 5 Comparison of properties of nanosphere obtained from three different residues

Conclusions

Heavy liquid residues from petroleum refining processes are an extremely desirable precursor for carbon materials, for both economical and environmental reasons. The continuous production of carbon nanospheres from FCC residues was demonstrated, representing a potentially suitable, low-cost method, similar to the long established production of carbon black. The process is highly dependent on temperature, with higher temperatures leading to higher yields, larger diameters and a higher oxidation resistance of the nanospheres.

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References

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- [2] Kiss LB, Söderlund J, Niklasson GA, Granqvist CG. New approach to the origin of lognormal size distributions of nanoparticles. *Nanotechnology* 1999, 10(1):25-28.