Carbon Products by Methane Decomposition with Organometallic Precursors

E. A. Scelzo*, F. Picca*, N. Molaro*, L. Basta, M. Commodo***, P. Minutolo***, A. D'Anna*.**

emanuelealberto.scelzo@unina.it

* Dipartimento di Ingegneria Chimica. dei Materiali e della Produzione Industriale (DICMaPI), Università di Napoli Federico II, P.le Tecchio 80, 80125, Napoli, Italy.

** Dipartimento di Fisica Ettore Pancini, Università di Napoli Federico II, Complesso Universitario di Monte S. Angelo, Edificio 6, Via Cinthia, 21, 80126, Napoli, Italy.

*** Istituto di Scienze e Tecnologie per L'Energia e La Mobilità Sostenibili, STEMS, CNR, P.le Tecchio 80, 80125, Napoli, Italy.

Abstract

This study investigates the properties of carbon particles generated during thermal methane decomposition in presence of ferrocene, an organometallic precursor used to catalyse the formation of carbon nanotubes. The process is carried out into a quartz tubular reactor heated to 925°C and ferrocene is sublimated in the upstream section. Carbon particles are collected on a substrate and subjected to detailed optical and chemical analyses, providing insights into their characteristics and highlighting notable differences arising from the presence of ferrocene. These findings contribute to optimizing methane pyrolysis and highlight the role of solid carbon in advancing sustainable hydrogen technologies.

Introduction

In the past years the interest in methane thermal decomposition has been growing thanks to the increasing demand for sustainable energy and advanced materials. This process allows to split methane into hydrogen and solid carbon [1]. A key factor for its scaling up is the control of carbon morphology and purity to enhance its value yielding diverse allotropic forms, e.g., amorphous carbon, graphite, and nanotubes. This requires an in-depth understanding of process parameters and carbon formation mechanisms. Recent studies have addressed kinetics, process optimization, and carbon characterization [2, 3]. Catalytic precursors are also used to promote methane decomposition and guide carbon nanostructures formation. Organometals like ferrocene ($Fe(C_5H_5)_2$) decompose at high temperatures, releasing iron nanoparticles in situ, which are highly active for methane pyrolysis, and act as seeds for nanotubes growth [4]. Typically, ferrocene is sublimed and pyrolyzed with a hydrocarbon carrier in a two-step furnace system, serving both as catalyst precursor and primary carbon source [4]. This study experimentally investigates carbon nanoparticle formation from methane and small amounts of ferrocene in a tubular flow reactor under pyrolytic conditions. A comparison with pure methane pyrolysis evaluates the influence of the precursor on carbon morphology and properties.

Methodology

High purity methane and nitrogen (40 mL/min, 25% CH_4, 75% N_2) are fed into a quartz tubular flow reactor (14 mm ID, 17 mm OD) inserted in an electric furnace set at 925 °C with a heated zone length of 18 cm. For experiments with ferrocene, a preheated line at 75±1 °C was added to sublimate ferrocene from a sample boat before the gases enter the reactor. Carbon particles were collected on a gold substrate at the reactor outlet. and on quartz supports in the reactive zone. Raman spectra were obtained with a Horiba XploRA Raman microscope (532 nm laser, 1.2 mW power).

Results

Fig. 1 shows the quartz tubes used in pyrolysis experiments without (A) and with (B) ferrocene. Raman spectra in the 750-2300 cm^{-1} range were recorded at different positions along the reactor either on quartz or on gold supports. In the absence of ferrocene, no deposition is observed on the internal walls of the reactor (case A). Since ferrocene decomposes at lower temperatures than methane, two distinct deposition times can be identified in case B, as evidenced both by the coloration and Raman spectra. At the reactor inlet, ferrocene undergoes pyrolysis first: the highly reactive cyclopentadienyl rings decompose rapidly at the lower temperatures met (zone 1). The related Raman spectrum shows a behavior similar to structures mainly composed by polycyclic aromatics. Progressing towards the center of the heated zone, a reddish deposit is found (zone 2), attributable to iron oxides such as hematite (Fe_2O_3) as confirmed by the Raman spectrum. Methane conversion in pyrolytic carbon predominantly occurs further downstream, resulting in silver/black deposits close to the reactor outlet (zone 3). The pyrolytic carbon produced with methane decomposition at the outlet of the reactor is compared to that produced with ferrocene and to a mature soot spectrum generated under rich flame conditions in the presence of an oxidizing agent (Fig. 2). The D-band of pyrolysis samples are both broader than the soot one, with a more remarkable difference in the ferrocene case.

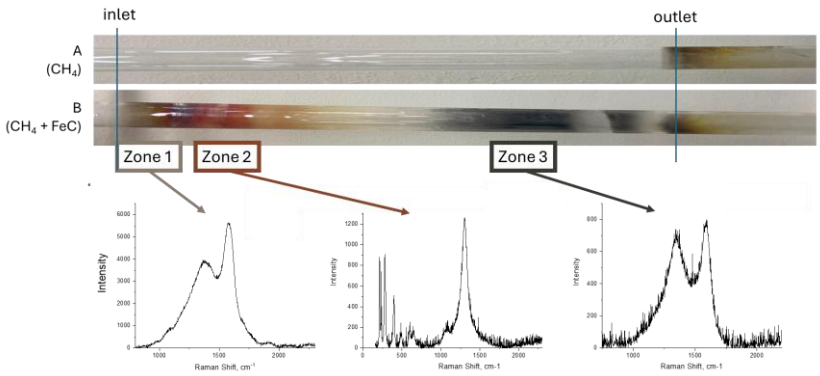

Figure 1. Tubular reactors after the decomposition in absence (A) and presence (B) of ferrocene. Adhered material Raman spectra at different positions are shown.

The ferrocene sample also shows an increased valley between the two main peaks. The small shoulder of the sample with ferrocene in the spectrum at the Raman shift of 1580 cm^{-1} might be related to an increase in the presence of graphitic domains. Anyway, the global structure of both pyrolysis samples remains amorphous.

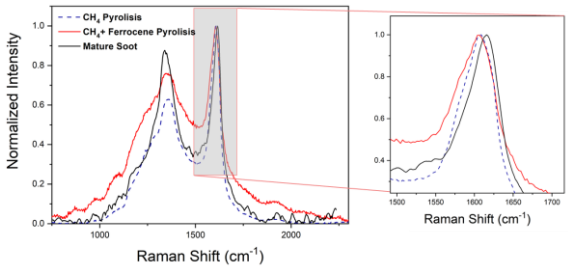

Figure 2. Raman spectra of pyrolytic products at the furnace outlet collected on gold substrates in presence and absence of ferrocene compared to mature soot.

Conclusions

Thermal methane decomposition was conducted at 925 °C in absence and in presence of ferrocene sublimated at 75 °C, that provides significant amounts of pyrolysis promoters, which either enhance carbon adhesion or accelerate methane decomposition. Raman Spectroscopy confirmed the presence of different carbon structures along the reactor. Further investigations involve the change in operating conditions, and the use of different precursors.

Acknowledgements

This material is based upon work supported by the 30 Air Force Office of Scientific Research under award 31 number FA8655-25-1-7003.

References

[1] Staffell, I., Scamman, D., Velazquez Abad, A., Balcombe, P., Dodds P. E., Ekins, P., Shah, N., Ward, K. R., "The role of hydrogen and fuel cells in the global energy system", *Energy Environ Sci* 12 463–491 (2019).

[2] Wang, Z. M., Zhang, X., Lei, J. M., Jin, K. R., Du-Wang, Tian, Z. Y., "Revisit the PAH and soot formation in high-temperature pyrolysis of methane", *J Anal Appl Pyrolysis* 1 182 106668 (2024).

[3] Naseri, A., Abbasi-Atibeh, E., Kiasadegh, M., Shen, J., Secanell, M., Semagina, N., & Olfert, J. S., "Characterization of particles generated by non-catalytic methane pyrolysis in a tubular flow reactor", *Aerosol Science and Technology*, *59*(2), 163-184 (2025).

[4] Yadav, M. D., Patwardhan, A. W., Joshi, J. B., & Dasgupta, K., "Kinetic study of multi-walled carbon nanotube synthesis by thermocatalytic decomposition of methane using floating catalyst chemical vapour deposition", *Chemical Engineering Journal*, *377*, 119895 (2019).