

# Nanostructured Carbon Materials

## Carbon Materials for Catalysis

### Carbon-Supported Metal Catalysts

**KEYWORDS:** Metal catalysts / Macrostructured / Carbon / Composite materials / Immobilization

Mono and bimetallic catalysts were synthesized through the combination of different metal active centers incorporated on an adequate carbon support.

Carbon nanotubes emerged as an efficient alternative to be applied as support due to their tunable properties, that contribute to enhancing their reactivity during catalytic reactions (namely  $\text{NO}_3^-$  and  $\text{BrO}_3^-$  catalytic reduction and  $\text{CO}_2$  methanation). Also, the possibility of combining these materials with metal oxides (known for their high reactivity) has enabled the synthesis of increasingly active and stable supports for application in catalytic reactions.

Some of the most active materials were incorporated on structured supports (cordierite monoliths) to be efficiently applied as support for the active metal phases for treatment in continuous catalytic systems.

#### Introduction

Carbon materials bring together the most desired properties for the design of remarkable supports: high specific surface area, inertness and stability under reaction conditions, suitable mechanical properties, availability of methods to easily perform changes in their chemical and physical composition and their regenerative potential. It is recognized that the support role is not just being a carrier for the metal phase, having a significant contribution in enhancing the activity of the catalyst and, to some extent, participating in the reaction mechanism. One of the main concerns when choosing an adequate support is related to the dispersion and stability of the metallic nanoparticles to obtain optimal performance and, somehow, decrease the amount of the costly metals that are usually used in this type of process.

The high specific surface area and well-developed porosity associated with the carbon materials are essential to promote higher dispersion of the metallic phase that will influence the activity and selectivity of the process.

Over the past few years, much time has been dedicated to studying carbon materials functionalization and modification to synthesize more active and stable supports for metal active centers.

#### Current Development

Under the scope of the present research topic, mono and bimetallic catalysts, supported on different supported materials, were synthesized with the objective of being applied for  $\text{BrO}_3^-$  and  $\text{NO}_3^-$  conversion.

Pd and Pd-Cu catalysts were synthesized on modified CNT (with tailored textural and chemical properties). Generally, the textural properties of the different synthesized supports strongly influenced the catalytic results obtained (mainly associated with the different metal dispersions achieved). In this work, the  $\text{pH}_{\text{pzc}}$  of the supports had an important effect on the catalytic process due to the electrostatic interactions between the support and the contaminant [1]. Generally, the supports presenting more basic groups (such as N-doped CNT) achieved the most interesting conversions. The N-groups incorporated on the carbon surface contribute with electrons to the electron system, increasing the electron density and the basicity of the carbon surface, thereby increasing its reductive character. On another hand, the application of oxidation

surface treatments to the carbon support would allow improvement in the dispersion of the metallic phases; a good dispersion will allow obtaining smaller and more isolated metallic particles that will actively participate in reaction (in detriment of larger particles resultant from their deposition on top of each other). However, for the specific case of the bimetallic catalyst, it is important to achieve a good compromise between the achieved dispersion and the interaction between the two metals since the weak interaction between the two phases could lead to partial deactivation of the catalyst (in the case of certain reactions).

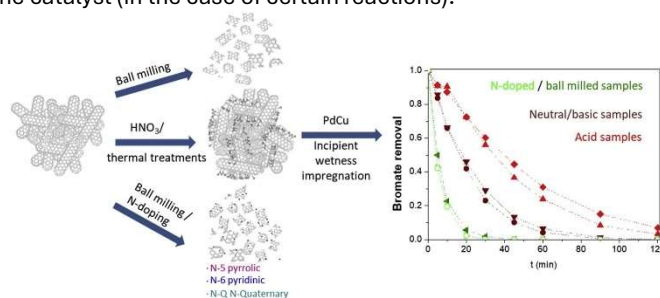


Fig 1. Influence of CNT immobilization on  $\text{BrO}_3^-$  catalytic results.

Incorporating these catalysts on structured supports (such as cordierite monolithic structures) is a necessary approach for applying this type of materials in large-scale catalytic processes. Related to this research topic, some works were carried out on the optimization of metallic phase incorporation for previous carbon-coated macrostructured catalysts. In these studies, different coating strategies and metal phase impregnation techniques were tested to optimize the synthesis process of macrostructured, mono/bimetallic catalysts, supported on carbon materials (carbon nanofibers and carbon nanotubes). Generally, different deposition strategies would lead to different rearrangements of metal nanoparticles on the carbon support (Fig 2) [2]. These rearrangements (considering the formation of metal alloys or not) are, also, strongly dependent on the used support since it plays an important role in the dispersion of metallic nanoparticles (as previously mentioned).

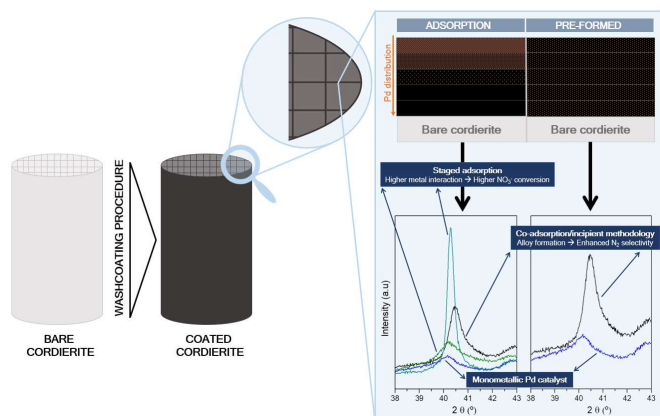


Fig 2. Bimetallic catalysts interaction depending on the immobilization technique adopted.

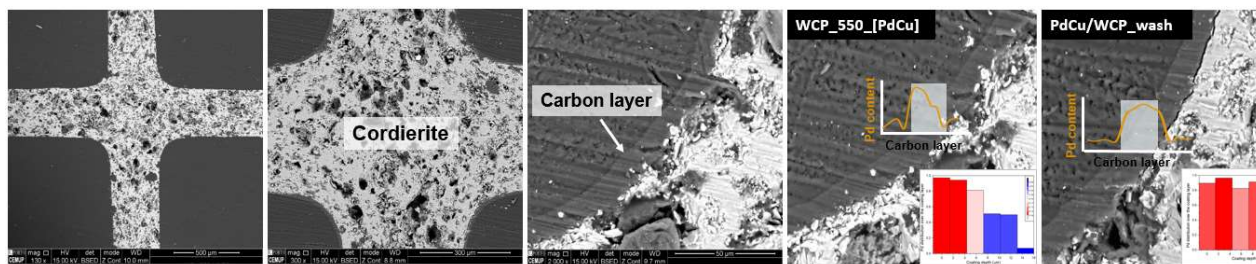


Fig 3. SEM images and Pd distribution over the carbon layer obtained for selected macrostructured catalysts for each of the synthesis

SEM images corresponding to the in-depth analysis of selected catalysts demonstrate that metal phase distribution through the coating layers is a decisive factor to obtain enhanced catalytic results. SEM experiments showed that the macrostructured catalysts synthesized through adsorption presented a less uniform distribution of the metallic phase, leading to its concentration in the outermost layers of the coating. In contrast, for the washcoating synthesized catalysts, a homogeneous distribution of the metallic phase was observed. This homogeneous distribution of the metallic phase along the coating layers proved to be a disadvantage for the specific case of oxyanions conversion through catalytic reduction (namely  $\text{NO}_3^-$  and  $\text{BrO}_3^-$ ) as it is difficult the reactant reaction with the metallic nanoparticles as they are present throughout the carbon layer down to greater depths (due to difficulties associated with reagents diffusion through the coating layer) [3].

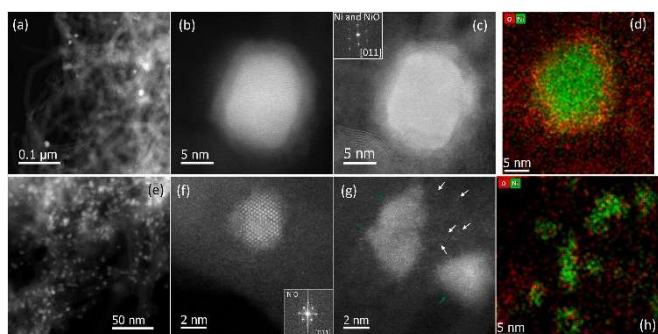


Fig 4. Representative low-magnification (a,e) and high-resolution (b,f,g) HAADF-STEM images and Fourier transform (FT) pattern [inset in panel (f)], together with high-resolution (c) ADF-STEM image and the corresponding STEM-EDX O and Ni mixture maps of the Ni/CNT (a-d) and Ni/CNT-N (e-h). The white arrows in (g) indicate the Ni single atoms and atom clusters, while the green arrows indicate the Ni nanoparticles [4].

In the field of gas-phase heterogeneous catalysis, carbon nanotubes (CNTs) have been intensively explored as catalysts themselves and, mainly, as supporting materials for the preparation of metallic catalysts. TEM images show that Ni/CNT-N consists of small catalyst nanoparticles with an average size of  $\approx 6$  nm that are well-dispersed over the N-doped CNTs. In contrast, the average size of catalyst nanoparticles supported on pristine CNTs is found to be significantly larger, namely,  $\approx 16$  nm. Moreover, the nanoparticles in the Ni/CNT catalyst exhibit agglomerated appearance. The observed difference in the size and dispersion of the catalytic nanoparticles over pristine and N-doped CNTs is also clearly seen during the comparison of the respective low-magnification HAADF-STEM images (Fig. 4). Furthermore, the fine microstructure of the catalyst nanoparticles in the Ni/CNT

and Ni/CNT-N catalysts was also found to be quite different. Specifically, the nanoparticles dispersed on the pristine CNTs in Ni/CNT exhibit Ni@NiO core-shell appearance (Fig. 4b,c,d). In contrast, small nanoparticles in Ni/CNT-N are mainly NiO (Fig. 4f,h).

When applied in the catalytic conversion of  $\text{CO}_2$  to  $\text{CH}_4$  the application of different materials for Ni support showed great importance since enhanced catalytic results were obtained for the catalyst supported on the functionalized support (Ni/CNT-N), showing the great importance that the support material presents for the catalytic reaction [4].

### Future Work

As future work for the present research topic some work has been carried out focused on the synthesis of composite materials (CNT together with different metal oxides) to be applied as supports for active metal phases. Also, taking into account the objective of achieving (as final step) the immobilization of the powder catalysts in structured supports, some experiments are being carried out focused on the study of new coating strategies that would allow an increase in the porosity, between the different coating layers, to facilitate the deposition of the active phases along the coating layer, and to increase the availability of surface contact for reaction in these structures.

### Related Sustainable Development Goals



### Outputs

#### PhD Theses

Liliana P. L. Gonçalves,  $\text{CO}_2$  Methanation over Bimetallic Catalysts supported on Carbon Materials with tailored surface properties, PDEQB, FEUP, 2022

#### Master Dissertations

João Manuel Cunha Bessa da Costa, Redução de bromato em efluentes reais com recurso a nanocatalisadores, MIEA, FEUP, 2021

#### Selected Publications

- [1] O.S.G.P. Soares, et al., J. Environ. Chem. Eng. 7 (2019) 103015.
- [2] A. S. G. Santos, et al., Environ. Technol. (2022).
- [3] A.S.G.G. Santos, et al., Appl. Catal. A Gen. 643 (2022) 118790.
- [4] L.P.L. Gonçalves, et al., Carbon 195 (2022) 35-43.

### Team

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### Funding

NanoCatRed: NORTE-01-0247-FEDER-045925, 2020-2023  
 LSRE-LCM Base Funding, UIDB/50020/2020, 2020-2023  
 LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023  
 LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019  
 LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984, 2013-2018  
 FCT Scholarships: SFRH/BD/128986/2017; UI/BD/151093/2021

### Related Sustainable Development Goals



## Outputs

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### Master Dissertations

Rita A. M. Barros, Carbon-based nanomaterials for the development of anti-leukemic drugs, MIB, FEUP, 2021

### Selected Publications

- [1] R. O. Cristóvão et al., Applied Sciences, 12, 17 (2022)
- [2] R. A. M. Barros et al., BioTech, 11, 2 (2022)
- [3] M. R. Almeida et al., Scientific Reports, 11, 21529 (2021)
- [4] R. O. Cristóvão et al., RSC Advances, 10, 52 (2020)

### Team

**Joaquim L. Faria**, Associate Professor; **Cláudia G. Silva**, Assistant Professor; **Raquel O. Cristóvão**, Assistant Researcher; **Maria A. Barros**, PhD Student; **Rita A. M. Barros**, PhD Student.

### Funding

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NanoPurAsp, POCI-01-0145-FEDER-031268, 2018-2022  
LSRE-LCM Base Funding, UIDB/50020/2020, 2020-2023  
LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023  
LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019  
LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984, 2013-2018  
FCT Scholarships: 2022.12055.BD, SFRH/BD/145014/2019

# Nanostructured Carbon Materials

## Carbon Materials for Catalysis

### Carbon as Catalyst

**KEYWORDS:** Carbon Materials / Metal-free catalysis / Basic Catalysis / Acid Catalysis

**Nitrogen-doped graphene flakes (GF) and reduced graphene oxide (rGO) materials were investigated in the reduction of 4-nitrophenol (4-NP) and the Knoevenagel condensation as model reactions.**

**Metal-free carbon nanotubes have been successfully used as catalysts in the oxidation of organic compounds.**

**Solid acid carbon xerogels were investigated as catalysts in the hydrolysis of cellulose and hemicelluloses. SO<sub>3</sub>H-bearing carbons prepared from sugars or glycerol were used as catalysts for the production of acetins via a transesterification route.**

#### Introduction

The development of metal-free catalysts to replace precious metals can represent a real breakthrough in catalytic processes. The use of metal-free catalysts can also avoid the common drawbacks of supported metal catalysts, like metal leaching and deactivation phenomena that traditionally occur in liquid-phase reactions. In this context, carbon materials are receiving an increasing scientific and industrial attention. They have been used as catalyst supports for many years, but they can also be used as catalysts on their own. High efficiency, environmental compatibility, low energy consumption, and corrosion resistance are some of the advantages that carbons offer compared with metal-based catalysts, in addition to high selectivity and long-term stability under mild conditions in many catalytic processes. Therefore, metal-free catalysts can become more cost-effective and eco-sustainable than metal-based catalysts.

Most of the carbon materials used in catalysis have a graphitic structure. The unsaturated carbon atoms at the edges of the graphene layers and at basal plane defects are able to react with different compounds containing O, N, H, Cl, S, B, P, etc., forming various types of surface functional groups. Such groups can play the role of active sites for catalysis, but they may also act as promoters or inhibitors, enhancing or diminishing the activity of the carbon catalyst, respectively. As a result, carbon materials have been reported to perform well in reactions typically catalysed by metals (such as dehydrogenations), non-stoichiometric oxides (such as oxidations and reductions) and acids (such as alkylation and dehydration).

#### Current Development

N-doped graphene catalysts Nitrogen doping of graphene flakes (GF) and reduced graphene oxide (rGO) was achieved through ball milling procedures with melamine and cyanuric chloride, followed by thermal treatments to 600 °C or 800 °C. Also, N-doped rGO was obtained by simultaneous reduction of graphite oxide in the presence of a N-precursor. N-doped GF was obtained with a maximum nitrogen amount of 2%, while N-doped rGO achieved a maximum of 10%. Different nitrogen species were found to be present on N-doped GF and rGO, namely pyridinic, pyrrolic, quaternary and pyridinic N-oxide.

Catalytic tests allowed the establishment of some relationships between the N-doped structural and composition properties and the catalytic activity:

i) N-doped GF was active in the catalytic reduction of 4-nitrophenol to 4-aminophenol with sodium borohydride (NaBH<sub>4</sub>), as illustrated in Fig.1.a. The results reveal that the basicity of the material allied to the presence of nitrogen atoms

affect positively the activity, since GF\_M800 and GF\_MC800 were the only samples significantly converting 4-NP to 4-AP. The high isoelectric points (IEP) alongside the presence of nitrogen heteroatoms were found to be the properties enhancing the activity (Fig.1.b).

ii) furthermore, N-doped rGO was tested on the Knoevenagel condensation of benzaldehyde with malononitrile (Fig2.a). This reaction is a C-C coupling reaction that requires a basic catalyst to occur and, therefore, it is frequently chosen as a reaction model to evaluate the catalytic properties of basic solid catalysts. Regarding nitrogen functionalized carbon nanomaterials, there are many reports on the use of these materials as basic catalysts for Knoevenagel condensation, essentially with amine functionalized fullerenes, carbon nanotubes and graphene. Nitrogen-doped carbon materials obtained by thermal treatments usually do not have amine groups. Instead, different N-sites contribute to their catalytic activity. There are few reports on the use of N-doped carbons in this reaction, and they usually emphasize the relevance of pyridinic-N groups as active sites. Instead, it was found that quaternary N-sites appear to be the most relevant nitrogen functionalities to promote the catalytic activity for this reaction. Fig.2.b shows the effect of the relative quantity of this type of nitrogen on the kinetic rate constant. It was also observed that large crystallite sizes and less amount of oxygen-containing surface groups contributed to the enhanced activity.

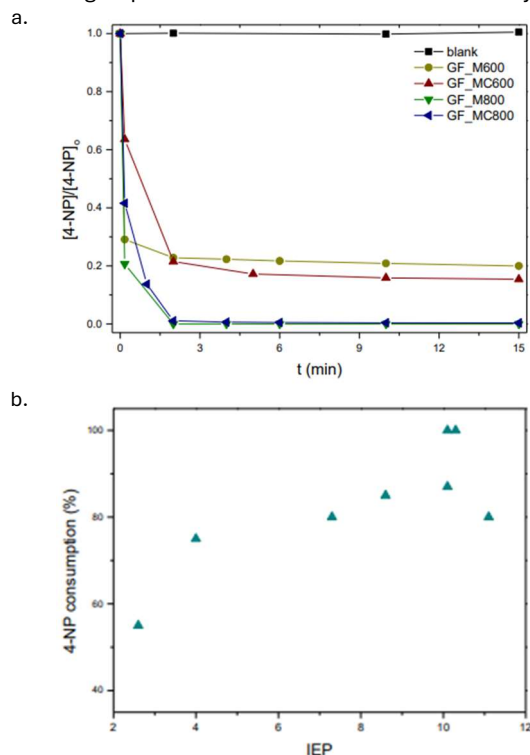


Fig.1 a) Evolution of the normalized 4-NP concentration as a function of time, t, of the uncatalyzed (blank) and catalyzed reactions (Room temperature; 30 mL of a 0.05 mmol L<sup>-1</sup> 4-NP solution, 56.65 mg of NaBH<sub>4</sub> and 30 mg of catalyst); b) 4-NP consumption as a function of the isoelectric point (IEP).

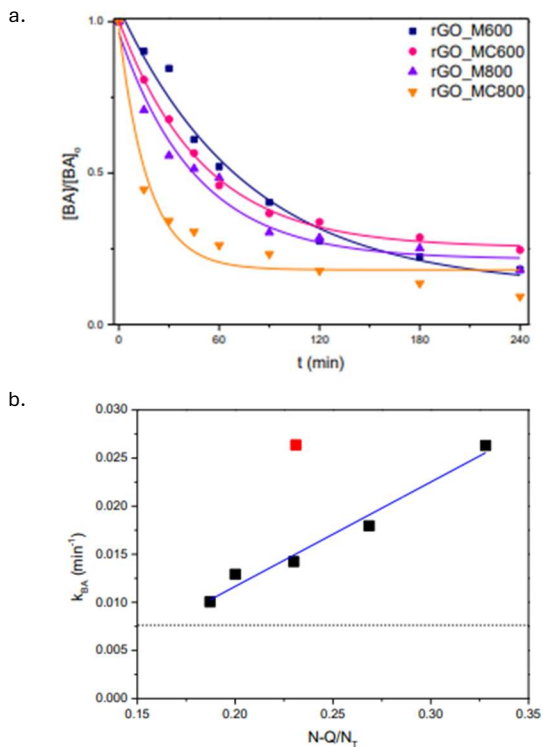


Fig.2 a) Evolution of the normalized benzaldehyde concentration as a function of time, t, (70 °C; 40 mg of catalyst; 5 mmol of benzaldehyde; 5 mmol of malononitrile in 10 mL of dimethylformamide (DMF)); b) Kinetic rate constant (k<sub>BA</sub>) as a function of the relative N-Q amount (N-Q/NT) (sample rGO\_MC800 highlighted in red).

Carbon catalysts for environmental applications Our previous research showed that active catalysts for the degradation of organic pollutants in the liquid phase with oxygen should have basic sites. The texture and the surface chemistry of carbon nanotubes (CNTs) were modified in the presence of adequate precursors (melamine, thiourea, sodium thiosulfate, sodium dihydrogen phosphate, and boric acid) of different heteroatoms (N, S, P, and B, respectively) [1-4]. Enhanced rates of oxidation of the model compounds (oxalic acid or phenol) were achieved in the presence of the N-doped samples, attributed to the presence of pyridinic and quaternary-N groups. In the presence of N-groups with unpaired electrons, such as the pyridinic groups, there is an electron donation effect which may enhance the adsorption of oxygen, improving the surface oxidation mechanism.

Acid catalysed reactions Esterification, etherification, hydration, hydrolysis, alkylation and isomerisation are well-known acid catalysed reactions. Carbon-based materials are also catalyst candidates for acid-catalysed reactions. Functionalization with acidic sites with suitable hydrophobicity and controllable wettability can greatly improve reactants adsorption and hydrophilic products desorption, enhancing activity, stability and reusability in a variety of organic substrates.

The hydrolysis of cellulose and hemicelluloses in the presence of solid acid catalysts is of great importance as an entry process for the production of biofuels and chemicals. The effect of carbon surface chemistry on the catalyst conversion and selectivity in hydrolysis of cellobiose to glucose was studied using solid catalysts based on carbon xerogels (CXs) containing various functionalities incorporating heteroatoms (S, P, N, O) [5]. CXs containing 3.4 wt% of phosphorus showed the best catalytic performance, reaching 90% conversion of cellobiose with 72% selectivity to glucose, under oxidative atmosphere and in a short reaction time of only 4 h. The presence of phosphonates (-P-C-) was found to increase the selectivity to glucose up to an unprecedented 87%. On the

contrary, carbonyls, quinones, pyridinic, pyrrolic and sulfonic groups were found to promote glucose degradation, leading to a final low yield of this product. Additionally, the increased concentration of oxygen in the reaction atmosphere was shown to significantly weaken the β (1-4)-glycosidic bond, increasing the final yield of glucose.

In a collaboration with the Faculty of Chemistry, Adam Mickiewicz University in Poland, SO<sub>3</sub>H-bearing carbons prepared from sugars or glycerol were used as catalysts for the production of acetins via a transesterification route. The efficient production of the target compounds, namely di and triacetins, which are valuable biofuel additives, was found to be strongly dependent on the content of sulfonic groups on the surface of these catalysts (Fig. 3). A direct correlation between -SO<sub>3</sub>H concentration and glycerol conversion, as well as the yield of higher esters was established.

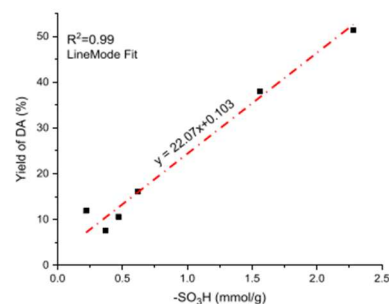


Fig.3. Yield of diacetins (DA) vs. the content of -SO<sub>3</sub>H groups for the glycerol transesterification with ethyl acetate performed over functionalized carbon catalysts.

### Future Work

Continuous efforts will be made to properly identify and quantify the active sites on carbon materials since this knowledge is mandatory to establish correlations with the catalytic activity, thus allowing for the correct benchmarking of the novel carbon catalysts.

Sulfonated carbon materials can be investigated in other acid catalysed reactions (alkylations, esterifications, acetalizations and hydrolyses).

### Related Sustainable Development Goals



### Outputs

#### PhD Theses

- [1] Raquel P. Rocha, Carbon Catalysts for Liquid Phase Reactions, PDEQB, FEUP, 2018.
- [2] Margarida Linhares, Nitrogen-doped graphene as metal free carbon-nanocatalysts, PDEQB, FEUP, 2018.

#### Selected Publications

- [1] Raquel P. Rocha et al., Topics in Catalysis 61, 1957 (2018).
- [2] O. Salomé G.P. Soares et al., Journal of Carbon Research, C, 5(2), 30 (2019).
- [3] Raquel P. Rocha et al., Catalysts 11(5), 578 (2021).
- [4] Raquel P. Rocha et al., Catalysis Today 356, 189 (2020).
- [5] Katarzyna M. Eblagon, ChemCatChem, 10, 4934 (2018).
- [6] A. Malaika et al., Fuel 304, 121381 (2021).

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#### Funding

POCI-01-0145-FEDER-006984  
 NORTE-01-0145-FEDER-000006  
 LSRE-LCM Base Funding, UIDB/50020/2020, 2020-2023  
 LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023  
 LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019  
 LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984, 2013-2018  
 FCT Scholarships: SFRH/BD/95411/2013, SFRH/BD/52620/2014  
 SFRH/BPD/110474/2015

# Nanostructured Carbon Materials

## Carbon Materials for Catalysis

### Multifunctional Catalysts for Synthetic Fuels Production

**KEYWORDS:** Fischer Tropsch / Carbon Materials / Cobalt Catalysts / Synthetic Fuels

**The ability to customize both the porous architecture and surface chemistry of carbon materials, not only during initial preparation but also through subsequent modifications, facilitates catalyst engineering for enhanced performance in Fischer-Tropsch synthesis. This enables heightened selectivity in the generation of targeted hydrocarbon groups, more specifically, the liquid range (C<sub>5-20</sub>).**

#### Introduction

Gas-to-Liquids (GtL) processes that convert natural gas or other gaseous hydrocarbons into longer-chain liquid hydrocarbons (e.g., jet fuel, gasoline or diesel) will be, in the near future, a decisive alternative to oil refining. These synthetic fuels can be processed into fuels of superior quality compared to those obtained by oil refining, leading to significant reductions in emissions of particles, NO<sub>x</sub>, SO<sub>x</sub>, and aromatics to levels lower than those found in oil-based fuels. These synthetic fuels are considered environmentally friendlier than fossil alternatives, and their production contributes to the carbon circular economy.

The Fischer-Tropsch (FT) reaction is at the core of the GtL process and is an alternative for transforming non-petroleum carbon resources into valuable chemicals, playing an essential role in producing sustainable and clean liquid fuels. However, the FT reaction still faces today's efficiency challenges, and the performance of FT is critical. It is a reaction that is generally performed in large-scale industrial GtL units using conventional fixed- or fluidized-bed reactors.

The primary motivation is to make an outstanding contribution to achieving more efficient GtL processes and developing new global technologies of national origin to promote the evolution of the future energy mix in a sustainable global environment. This study presents the exploration and advancement of an innovative catalytic solution (catalyst development) aimed at the continuous production of premium fuels. The objective is to surpass the efficiency of existing methods employed in conventional GtL plants. Significant innovation is anticipated through a creative design approach, enabling thorough examination and optimization of the impact of engineered multifunctional materials.

The selection of the support for the catalyst is critical as it helps to disperse the active metal phase, and metal-support interactions have a profound impact on the resulting performance of the catalyst. Through precise customization of the catalyst formulation, there is a resultant enhancement in activity, directly influencing operational parameters such as reduced reaction temperatures and pressures. This ultimately leads to energy savings, a significant cost factor in large-scale chemical processes. The most used supports in FT include metal oxides and carbon-based materials. Carbon-based materials possess the advantage of good thermal conductivity, high specific surface area, and high thermal and chemical stability under middle operation conditions. Furthermore, these materials allow for modification during synthesis or through subsequent treatments. The idea of chemically modifying the surface of these supports, creating multifunctional catalysts, attracts increasing attention because by changing the surface of the

support, we can influence other FT parameters, and with the proper catalyst formulation, it may be possible to selectively direct the reaction towards the desired products, liquid hydrocarbons (C<sub>5</sub>-C<sub>20</sub>), while reducing the number of reactants wasted, forming unwanted by-products.

Furthermore, the use of different reaction media and reactor types can further influence the performance of the catalysts, opening possibilities for industrial and large-scale applications.

#### Current Development

This work has been carried out under a collaboration with Prof. Helder T. Gomes (IPB – Polytechnic Institute of Bragança, Portugal). Various multifunctional catalysts for use in the FT reaction were developed. The research was centred on the production and modification of the catalyst supports through diverse treatments. The materials exhibited characteristics that endowed them with the ability to function as catalysts, predominantly producing the liquid range of hydrocarbons with minimal generation of CO<sub>2</sub> and waxes. The focus of the study was on tailoring the catalyst supports to enhance their catalytic properties and optimize the desired product spectrum. The resulting catalysts demonstrated remarkable selectivity and stability over extended reaction periods, making them promising candidates for efficient and sustainable FT synthesis.

Various carbon materials with diverse treatments have been tested as supports for the catalyst with cobalt as the active metal (with/out the presence of rhenium as a promoter). The impregnation of the support with the cobalt was accomplished through incipient wetness impregnation (IWI). The produced catalysts were evaluated in FT reaction for synthetic fuel production, with a focus on the production of the liquid range of hydrocarbons, specifically Jet Fuel (C<sub>12-15</sub>), while minimizing the production of gases (C<sub>1-4</sub>) and waxes. Before being tested in the FT reaction, each catalyst was reduced to the appropriate temperature, as determined through characterization. The reactions were conducted using a fixed-bed reactor (Microactivity Effi, MAE, from PID

Table 1. Product selectivities for the produced catalysts

Catalyst	Selectivity (%)					
	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>5</sub> -C <sub>11</sub>	C <sub>12</sub> -C <sub>20</sub>	C <sub>21+</sub>
Co/CNTF1	<1	9.5	2.3	42.0	43.2	2.4
Co/CNTF2	<1	11.2	2.4	40.2	42.7	3.0
Co/N-CNTF3	<1	8.0	2.1	37.3	46.6	5.6
Co/N-CNTF4	<1	9.3	2.5	41.4	41.5	4.7
Co/CNTFcalc350	<1	6.2	1.6	38.2	50.5	2.9
Co/CNTFcalc550	<1	5.9	2.1	44.2	45.5	1.6
Co/CNTFcalc750	<1	5.4	2.5	55.4	34.4	1.7
Co/CNTFcalc900	<1	1.7	1.1	36.6	55.3	4.8
Co/CNF	<1	3.5	1.6	40.3	48.5	5.8
Co/FLGF	<1	2.3	1.4	34.9	55.9	5.3

Eng&Tech) in collaboration with CoLAB Net4CO<sub>2</sub>. The reactor was fed with a synthesis gas composed of carbon monoxide, hydrogen and nitrogen with a Gas Hourly Space Velocity (GHSV) of 4 m<sup>3</sup>·kg<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup> at 220 °C and 20 bar. The standard

reactions were conducted for a duration of 28 hours. The catalytic tests were carried out using the best operating conditions for fixed-bed reactors, which were identified after a detailed parametric study where the influence of pressure, temperature and GHSV was successfully evaluated. The gaseous products were examined using an online GC (YL6500, YL instrument CO. LTD), fitted with two columns and a TCD, using Helium as the carrier gas during the course of the reaction. The liquid products obtained were collected after the reaction had concluded and were analyzed using an offline GC equipped with a Supelcowax 10 capillary GC column with a flame ionization detector (FID) and using Helium as the carrier gas. The catalytic tests performed served as a basis for the optimization of the catalysts that were produced, as well as for the scale-up of the process using different reaction media and reactor configurations.

Efforts were also made to develop catalysts with dual functionalities with carbon materials. Various carbon materials were employed, including nanotubes (CNT), nanofibers (CNF), and graphene (FLG). CNF and FLG underwent only acid functionalization, whereas CNTs underwent chemical and/or thermal treatments. The functionalization (acidic and thermal) of the supports was employed to incorporate different groups onto the support surface, aiming to enhance performance. In this study, it was shown that the performance of carbon-supported cobalt catalysts for FT can be dictated by the modifications in the surface chemistry. The supports that underwent functionalization had outstanding performances compared to their pristine counterparts. All the produced carbon-supported catalysts showed excellent selectivity for the desired range.

The catalysts produced with the new supports proved to be efficient in producing the desired range ( $C_{5-20}$ ) while generating a reduced amount of gaseous hydrocarbons ( $C_{2-4}$ ) and waxes ( $C_{21+}$ ), as shown in Table 1. These results establish a potential future direction for the production of synthetic fuels.

In addition to the good selectivity exhibited by the catalysts, another observed characteristic in the produced catalysts is that they displayed excellent stability during long-duration reactions. To assess stability, the catalysts were subjected to a long-duration reaction lasting 100 hours in a fixed-bed reactor using the optimal conditions. They showed no variation in product distribution throughout the reaction. This stability in performance and selectivity is noteworthy for potential applications on an industrial scale.

Supports and catalysts produced were also characterized using various techniques such as  $NH_3$  temperature-programmed desorption, thermogravimetric analysis and differential scanning calorimetry, inductively coupled plasma optical emission spectroscopy,  $H_2$  temperature-programmed reduction, transmission electron microscopy (TEM) and scanning transmission electronic microscopy. Figure 1 shows the transmission electron microscopy (TEM) of two of the produced catalysts. This analysis was conducted to determine cobalt particle size distribution and the morphology of catalysts,

It can be seen from the images that the cobalt was successfully impregnated in the support, and most of the Co particles were confined inside the CNTs when these were functionalized with acid, with sizes ranging between 3-5 nm.

## Future Work

Further investigation is required to thoroughly examine the impacts of various modifications and catalyst designs, particularly concerning the application of modified catalysts in various reaction media, such as biphasic systems, as this

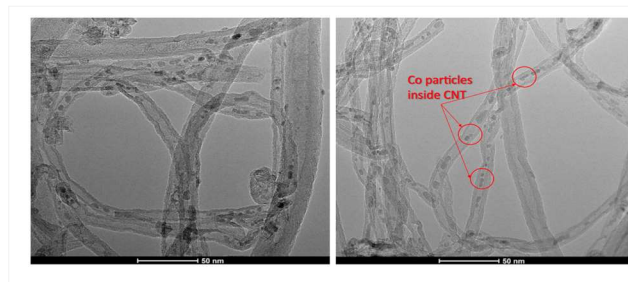


Fig 1. Transmission electron microscopy of the produced Co/CNTF catalyst. A: CoRe/Pural; B: Co/CNTF1.

is also a parameter that can influence reaction outcomes and can further enhance selectivity for the desired range of hydrocarbons.

Once the best catalysts have been identified, the next step will be their application in a new type of reactor, the NetMIX technology. The FT reaction is severely constrained by the low interfacial areas achieved with currently used industry-standard reactors and the reduced heat/mass transfer coefficients, resulting in poor catalyst performance. The application of the NetMIX reactor technology initially developed at the University of Porto will help overcome these limitations. This technology is based on a unique micro/mesoreactor topology formed by a network of interconnected static mixing chambers through transport channels, enabling optimized and reproducible fluid mixing. The additional oscillatory solid dynamics of the reactive flows increase micromixing capacity, potentially leading to a continuous sweeping of the catalyst surface, minimizing the presence of stagnant zones and mitigating potential deactivation. Using this modular technology will result in net improvements directly impacting the operating conditions, such as lowering the temperature and pressure at which the FT reaction occurs. These results will affect the chain of value in fuel production, with significant savings towards consumer consumption at various levels while promoting decarbonization strategies. In addition, this technology offers ease of scale-up and opens doors to potential industrial applications.

## Related Sustainable Development Goals



## Outputs

### PhD Theses

Thais Sayuri Berberich, Multifunctional catalysts for improved Fischer-Tropsch synthesis using NetMIX-based microreactor technology towards the competitive production of synthetic fuels, PDEQB/PDEA, FEUP, ongoing

### Master Dissertations

David Faria Aguililar, Emerging catalytic systems for the Sustainable production of synthetic Fuels, MIEQ/MIEA, FEUP, 2023

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### Funding

Cat4GtL - POCI-01-0247-FEDER-069953, co-funded by the European Regional Development Fund (ERDF) through COMPETE 2020 under PORTUGAL 2020 Partnership Agreement.

LSRE-LCM Base Funding, UIDB/50020/2020, 2020-2023

LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023

LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019

LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984, 2013-2018