



# Article Copper Supported on Mesoporous Structured Catalysts for NO Reduction

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**Abstract:** Nitrogen oxides (NO<sub>x</sub>) are one of the pollutants of greatest concern in terms of atmospheric contamination and, consequently, human health. The main objective of this work, is the synthesis of structured carbon catalysts, introducing on their surface metals and nitrogen groups, catalytically active in NO reduction. Structured catalysts represent an attractive alternative to powder catalysts because they have better thermal stability and lower pressure drop. The catalysts were synthesized by coating a melamine foam using precursor solutions of carbon xerogels with and without nitrogen (using melamine and urea as precursors), and impregnated with transition metals (Fe, Ni and Cu). The introduction of nitrogen and metals modified the textural properties of the materials. Samples synthesized with melamine presented the highest amount of nitrogen, while the highest content of copper, found to be the most active transition metal for NO reduction, was found in structured catalysts impregnated with urea. The presence of transition metals in catalysts is essential for the reduction of NO to N<sub>2</sub> and the introduction of nitrogenous precursors makes this evident. The synthesis and application of carbon-supported structured catalysts containing transition metals for NO reduction is demonstrated in this work for the first time, as well as the study of the factors influencing their performance.

Keywords: nitric oxide; catalytic reduction; structured catalyst; carbon; transition metal catalyst; SCR

## 1. Introduction

Pollution is one of the problems with significant impact in the 21st century caused by excessive human consumption, directly affecting the climate, the quality of drinking water, agricultural production and, consequently, the health of living beings. Nitrogen oxides ( $NO_x$ ) are considered one of the pollutants that cause the greatest concerns in terms of atmospheric contamination, as they contribute to photochemical smog, acid rain, degradation of the ozone layer and the greenhouse effect [1]. Nitrogen monoxide (NO) represents about 95% of the total nitrogen oxides emitted and is a colorless and odorless gas that is released into the atmosphere due to incomplete combustion processes of fuels used in stationary and mobile sources [2].

Several measures have been applied to reduce their emissions, essentially in the chemical and transport industries, to prevent these gases from being emitted into the atmosphere. The methods used to reduce  $NO_x$  emission are divided into two main groups: primary and secondary methods. The former reduce  $NO_x$  emissions by up to 50% and are preventive measures that consist of changing operating conditions and organizing the process during pre-combustion and combustion [3]. The latter are applied after combustion and reduce up to 100% of the nitrogen oxides already formed [2].



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Secondary measures for NO<sub>x</sub> elimination include selective catalytic reduction (SCR), where NO is directly reduced to N<sub>2</sub> using different external reducing agents over different catalysts such as ammonia over a modified zeolite [4], V/Mo-Ti [5] and V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-carbon nanotube [6], urea over activated carbon supported metal oxide [7], hydrocarbons [8], hydrogen [9] or carbon materials, where carbon acts as a reducing agent, support and catalyst (Equations (1) and (2)) [10,11].

$$2NO + C \rightarrow N_2 + CO_2 \tag{1}$$

$$2NO + 2C \rightarrow N_2 + 2CO \tag{2}$$

The use of carbon in SCR makes the process more economical and environmentally friendly; however, it presents as disadvantages the need to reach temperatures above 500 °C for conversion to occur, which causes the consumption of carbon by combustion at high levels of oxygen [11,12]. Reducing the reaction temperature proved to be the most effective method to minimize carbon combustion by  $O_2$ , which simultaneously affects the catalytic performance [11].

The use of transition and alkali metals in carbon-based catalysts significantly reduces the activation energy of the reactions and increases the adsorption capacity of NO [13]. During the reaction of NO with carbon, the impregnated metal participates in the redox mechanism, being oxidized by NO and reduced by carbon [14]. E. Bailón-García et al. [14] prepared metal (Fe, Co, and Cu) catalysts dispersed on carbon xerogels to study the activity of the materials in NO<sub>x</sub> reduction and verified that the complete NO conversion, with the highest selectivity, was attained at 230 °C in the presence of Cu.

Nitrogen doping of carbon materials increases the surface electrons density and the ability to donate them, which results in a better performance of the catalysts [15], improving the catalytic and adsorbent properties of activated carbons for  $SO_x$ ,  $NO_x$  and  $CO_2$  [16,17]. In the case of carbon xerogel (CX), nitrogen doping can be accomplished by introducing a nitrogen-containing precursor into the formation of the organic structure of the carbon xerogel through sol-gel polycondensation [17]. Activation or impregnation with transition metals and/or conductive polymers can facilitate the incorporation of the nitrogen atom into the carbon matrix to form more active nitrogen-carbon structures with high surface area, enhancing the catalytic performance of the carbon material [11,13–15,18–20].

Monolithic structured catalysts are highly porous and have a structure of uniform and random blocks consisting of narrow channels in parallel or zigzag [21,22]. They can be ceramic or metallic structures. Ceramics show better porosity, good adhesion to the coating and thermal stability, while metallic ones show better heat transfer, mechanical stability, wall thickness and total volume [21]. Foams are another type of structured catalyst characterized as either "closed cell", where the cells are connected through solid faces, or "open cell", which have solid margins and open faces, that allows the fluid transfer from one cell to the other decreasing the flow resistance. Therefore, catalysts in the form of "closed cell" foams are more favorable to catalysis processes [23]. Melamine foam (MF) is a type of ultra-fine fiber foam and has the benefits of low bulk density, high density structure and flexibility, excellent mechanical properties and porous structure, even after high temperature carbonization [18]. These structures, not catalytically active, serve as a support to give rise to a structured catalyst prepared by coating an active catalytic phase. The method of synthesis of the structured catalyst is a major factor in the properties and efficiency of the catalysts to be obtained, and some examples are precipitation, impregnation, lyophilization and sol-gel polycondensation [24].

The focus of this work was the preparation of structured catalysts based on carbon materials, which represent an attractive alternative to conventional powder catalysts because they have better heat and mass transfer, reduced pressure drop and superior thermal and mechanical stability [21,25–27]. The primary objective is the synthesis of structured carbon catalysts catalytically active in the reduction of NO. These catalysts were synthesized by coating melamine foams and cordierite monoliths (CM) using precursor solutions of

nitrogen-free and nitrogen-doped carbon xerogels. Initially, the performance of the carbon catalysts in powder form was assessed in NO reduction where the characteristics of the carbon and N-doped carbon xerogels were assessed. The more active catalysts were then impregnated with transition metals (Fe, Ni, and Cu). Then, the best performing samples were prepared as structured catalysts by coating melamine foams and cordierite monoliths.

## 2. Results and Discussion

## 2.1. Catalysts Characterization

Table 1 shows the textural properties of the synthesized materials in terms of specific surface area ( $S_{BET}$ ), specific surface area of mesopores ( $S_{meso}$ ), specific volume of micropores ( $V_{micro}$ ) and total pore volume ( $V_p$ ).

Sample	$S_{\rm BET}/{\rm m}^2~{\rm g}^{-1}$	$S_{\rm meso}/{\rm m}^2~{\rm g}^{-1}$	$V_{ m micro}/ m cm^3~g^{-1}$	$V_{\rm p \ p/po \ = \ 0.95}/{\rm cm^3 \ g^{-1}}$
CX	636	211	0.17	1.30
CX_Fe	628	203	0.17	1.30
CX_Ni	599	199	0.16	1.30
CX_Cu	590	182	0.17	1.30
CX_M_Cu	524	55	0.19	0.29
CX_U_Cu	404	79	0.14	0.20
MF_10Cu	614	199	0.17	0.89
MF_M_10Cu	542	65	0.20	0.28
MF_U_10Cu	796	140	0.27	0.35
MF_U_20Cu	536	140	0.18	0.40
MF_U_30Cu	471	48	0.18	0.22
CM_U_10Cu	71	8	0.03	0.04

Table 1. Textural properties of the catalytic materials.

Values obtained by total catalyst mass.

The original CX demonstrates the highest specific surface area, 636 m<sup>2</sup> g<sup>-1</sup>. The  $S_{\text{BET}}$  decreased after impregnation with Fe, Ni and Cu, respectively, and the micropore volumes did not change significantly. This phenomenon is due to the introduction of the metals, which partially block the pores, making part of the CX surface inaccessible for N<sub>2</sub> adsorption [10]. Samples synthesized with nitrogen precursors and impregnated with copper also showed a decrease in specific surface areas due to blocking of access to the surface porosity during analysis [28].

The MF\_10Cu (without nitrogen) sample presents a  $S_{BET}$  of 614 m<sup>2</sup> g<sup>-1</sup> and the CX\_Cu of 590 m<sup>2</sup> g<sup>-1</sup>, while for the MF\_M\_10Cu (prepared with melamine) and in CX\_M\_Cu it corresponds, respectively, to 542 m<sup>2</sup> g<sup>-1</sup> and 524 m<sup>2</sup> g<sup>-1</sup>. However, in MF\_U\_10Cu (synthesized with urea) the  $S_{BET}$  is 796 m<sup>2</sup> g<sup>-1</sup>, which differs considerably from the obtained for the respective CX\_U\_Cu, 404 m<sup>2</sup> g<sup>-1</sup>, which must be related to the strong adhesion of urea to the structured materials due to the urea-melamine-formaldehyde interaction generated during the impregnation of the carbon xerogel solution with urea in the melamine foam [27–29].

The specific surface areas and the volume of micropores decreased with the increase in the amount of metal, which partially block the pores, making part of the CX surface inaccessible for N<sub>2</sub> adsorption [10,11]. In contrast, the CM\_U\_10Cu presents the lowest  $S_{\text{BET}}$  and the micropore volume almost zero, due to the contribution of the CM support, since it has a specific surface area of 1 m<sup>2</sup> g<sup>-1</sup> [27].

The introduction of the nitrogen precursor, urea or melamine, during the synthesis of CX allows obtaining materials with nitrogen in their structure, 2.1 and 4.9% (wt.%), respectively, for sample CX\_U and CX\_M. The increase in the nitrogen amount in the melaminedoped sample can be explained by the fact that the molecular structure of melamine allows the incorporation of more N-functionalities when compared with urea [30].

The copper content determined through ICP-OES for each sample is listed in Table 2.

Sample	% <sub>ICP-OES</sub> Cu	% <sub>XPS</sub> Cu	% <sub>XPS</sub> N
CX_M	-	-	2.3
CX_U	-	-	1.4
CX_Cu	14	-	-
MF_10Cu	3.3	0.98	-
MF_M_10Cu	4.6	1.3	3.2
MF_U_10Cu	6.7	1.5	2.3
MF_U_20Cu	9.4	-	2.3
MF_U_30Cu	17	-	2.3
CM_U_10Cu	3.1	-	-

Table 2. Copper and nitrogen content determined by ICP-OES and XPS.

Values obtained by total catalyst mass.

In CX powders, the difference of the 14% Cu obtained through ICP-OES from the expected 10% Cu is associated with deviations in the synthesis. The percentage of copper in the structured catalysts increases in the order MF\_10Cu < MF\_M\_10Cu < MF\_U\_10Cu, revealing that MF\_U\_10Cu demonstrates the greatest capacity for copper impregnation, as it has a higher specific surface area than the other MF [31]. As expected, in materials where 20 and 30% Cu was impregnated, the percentages obtained were higher than those obtained for MF\_U\_10Cu.

The surface composition analyzed by XPS (Table 2) revealed a similar trend to that obtained through EA and ICP-OES, since the highest percentage of nitrogen is verified in samples with melamine, and the amount of copper also increases in the order MF\_10Cu < MF\_M\_10Cu < MF\_U\_10Cu. However, the results obtained through this analysis are lower than those obtained previously, which can be explained by the fact that this technique provides information on the elemental composition and nature of chemical bonds of atoms on the surface of materials (up to 10–15 nm), revealing that nitrogen and copper are not homogeneously distributed on the surface and the bulk of the MF. Concerning N-functionalities, quaternary nitrogen (QN), pyrrolic (N5) and pyridine (N6) groups are typical structures formed in carbon materials prepared between 550 and 900 °C [32].

Thermogravimetric analyses were performed under an air flow up to 900 °C for CX (Figure 1a) and MF (Figure 1b) to determine the thermal stability of the catalysts.



Figure 1. Weight loss during thermogravimetric analysis of (a) CX and (b) MF.

In the original CX there is a loss of mass starting from 440 °C, while in CX\_M and CX\_U combustion starts at 460 and 520 °C, respectively. Complete combustion of the samples occurs above 600 °C in CX without nitrogen and above 750 °C in CX\_M and CX\_U. XPS analysis reveals no significant differences regarding the type of nitrogen groups; therefore, the introduction of these groups in the CX, either with melamine or urea as a precursor, gives thermal stability to the materials in an oxidizing atmosphere and the differences are related to the amount of nitrogen present in the materials [33]. Combustion of CX\_10Cu,

CX\_M\_10Cu and CX\_U\_10Cu started at 260 °C, a value considerably lower than that of CX, CX\_M and CX\_U, while the gradual increase in Cu content led to slighter changes in combustion temperature. These results suggest that there is an interaction between O<sub>2</sub> present in the air and copper, leading to a burn of the sample at lower temperatures [34]. MF samples were found to be stable up to 350 °C, suggesting that the structured catalysts were more thermally stable than their powder CX counterparts, with combustion starting at 260 °C [21,25].

Figure 2 shows the images obtained through scanning electron microscopy of an as-received foam (Figure 2a) and the foams that were in contact with the nitrogen-free CX solution (Figure 2b,c), with melamine (Figure 2d) and with urea (Figure 2e).



Figure 2. SEM images of (a) MF, (b) and (c) MF\_10Cu, (d) MF\_M\_10Cu and (e) MF\_U\_10Cu.

As expected, all samples have similar morphologies [17]. Figure 2a shows the structure of the foam without any coating. In Figure 2b,d,e, this structure is covered by the respective CX solutions. As mentioned by other authors, it is proven that CX is made up of interconnected spherical particles (circled), and the MFs have a porous structure in the shape of a honeycomb [34,35]. Figure 2c shows bright spots (marked with arrows) corresponding to the copper particles, which indicates a homogeneous copper distribution throughout the matrix.

## 2.2. *Catalytic Tests*

# 2.2.1. Powder Catalysts

Blank tests (without catalyst) were carried out to evaluate the influence of the geometry of the reactors used for powder catalysts (CX) and structured catalysts (MF and CM), with diameters of 0.7 and 2.6 cm, respectively. The homogeneous conversion of NO (Figure A1) was also assessed and differs only 1% between the two tests, being 14% for the 0.7 cm reactor and 13% for the 2.6 cm reactor (Appendix A).

The impregnation of metals on carbon-based catalysts increases the adsorption capacity of NO in the materials and reduces the reaction temperature significantly [13,14]. Accordingly, the catalytic performance of Fe, Ni and Cu supported on CX was assessed in the reduction of NO.

In Figure 3 it can be seen that the CX prepared without metals does not show significant activity in the catalytic reduction of NO up to the maximum temperature used in this study, 350 °C, and the transition metals studied were able to reduce NO into N<sub>2</sub> through carbon in the presence of oxygen [11,12]. The CX\_Fe and CX\_Ni samples showed a maximum conversion of 56 and 54%, respectively, for the maximum reaction temperature, and the sample CX\_Cu showed complete conversion at 324 °C. Illán-Gómez et al. [20] studied the catalytic reduction of NO<sub>x</sub> through transition metals (Fe, Co, Ni and Cu) on a carbon support and the effect of oxygen on catalytic properties of metals at 300 °C, reporting identical values (14, 26 and 44% at 300 °C for Fe, Ni and Cu, respectively), but slightly lower, than those presented in this work. The catalytic activity of the metal for the NO reduction by carbon is affected by the tendency of the metal to be oxidized by NO and by the ease of the resulting metal oxide of being reduced by carbon [20]. Although the largest specific surface area is verified in CX\_Fe (628 m<sup>2</sup> g<sup>-1</sup>) and the smallest in CX\_Cu (590 m<sup>2</sup> g<sup>-1</sup>), the copper impregnated material exhibited better catalytic performance for NO reduction [14].



**Figure 3.** NO concentration in the presence of CX with metals with [NO] = 1000 ppm in He with 5% of O<sub>2</sub>.

#### 2.2.2. Powder N-Doped Catalysts

All copper-based materials presented high conversion values than their metal-free counterparts (Figure 4); however, only those supported on CX and CX\_M showed 100% conversion below the maximum reaction temperature of 350 °C. CX\_Cu achieves full conversion at 324 °C, the CX\_U\_Cu sample allows 90% to be obtained at 332 °C and the CX\_M\_Cu achieves 100% conversion at 329 °C.



**Figure 4.** NO concentration in the presence of CX and CX\_N with and without metals with [NO] = 1000 ppm in He with 5% of O<sub>2</sub>.

The influence of the specific surface area and the amount of nitrogen was assessed in Figure 5. As all materials have the same amount of copper, samples are more catalytically active the greater the specific surface area and the greater the percentage of nitrogen in the CX [31].



**Figure 5.** NO concentration in the presence of CX and CX\_N with copper with [NO] = 1000 ppm in He with 5% of O<sub>2</sub> as a function of the specific surface area and the amount of nitrogen.

# 2.2.3. Structured Catalysts

Figure 6 shows the profiles obtained in the NO reduction reaction by catalysts structured with MF at 350  $^{\circ}$ C.

Table 3 summarizes the conversions obtained by the MF samples at 350 °C, the amount of the structured catalysts used in the reactions and the conversions as a function of these values, the specific surface area and the copper mass are also listed.



Figure 6. NO concentration in the presence of MF with [NO] = 1000 ppm in He with 5% of  $O_2$ .

Sample	$x_{\rm NO} (T = 350 ^{\circ}{\rm C})^{/\%}$	m <sub>MF</sub> /g	$C_{ m NOred}/ m mmol~g^{-1}$	$C_{ m NOred}  imes 10^{-3}/ m mmol\ m^{-2}$	$C_{\rm NOred}/\rm mmol~g_{Cu}^{-1}$
MF_10Cu	35	2.58	0.45	0.74	13.6
MF_M_10Cu	90	3.95	0.76	1.40	16.6
MF_U_10Cu	94	2.92	1.07	1.35	17.1

NO conversions were determined as a function of mmol of NO per gram of foam  $(mmol g^{-1})$  since the mass of each MF under study is slightly different; therefore, in Figure 6, it can be seen that MF\_10Cu achieves a very different conversion value while MF\_M\_10Cu and MF\_U\_10Cu exhibit similar profiles and the maximum conversion is close to each other. The achievement of these results is due to the fact that doping carbon materials with nitrogen increases the density of electrons and the ability to donate them, which results in a better catalytic activity [15]. Other authors carried out studies on the oxidation of NO and also proved that materials with nitrogen promote NO adsorption [17,26,36,37]. In Table 3, it is clear that MF U Cu stands out in the catalytic activity of reducing NO in relation to MF\_M\_10Cu and MF\_10Cu, since this material was able to reduce 1.07 mmol  $g^{-1}$ . The converted amount of NO per specific surface area increases from MF prepared without nitrogen solution to MF synthetized with nitrogen solution. However, the specific surface area value decreases when melamine is impregnated and increases when urea is introduced into the MF structure. Moreover, the intrinsic activity of the copper on the urea doped sample is higher than the remaining, revealing an improved interaction between surface nitrogen species and the metal catalyst using this precursor. These results reveal that factors such as specific surface area, amount of copper, amount of oxygen and amount of catalyst have influence in the catalytic results.

To determine if higher amounts of copper results in better catalytic activity in reducing NO, experiments were carried out with MF\_U with 10, 20 and 30% Cu. These contents correspond to the amount of copper placed in the solution as a function of the mass of the MF; however, as the sample does not fully adsorb all copper in the solution, the MF samples have an amount of copper lower than expected (Table 2).

According to the data presented in Figure 7, the temperature required to reach the same NO conversion value decreases with the increasing content of copper in the MF. In MF\_U\_20Cu and MF\_U\_30Cu, the NO reduction curves are identical, with a mismatch between them caused at low temperatures by the chemically adsorbed  $O_2$  on the surface and at high temperatures due to the better performance in the conversion of NO with the

increase in the amount of copper in the sample [38]. This confirms that the presence of Cu is important as the greater the amount of copper in the catalysts the better the catalytic performance for NO reduction.



**Figure 7.** NO concentration in the presence of samples with 10, 20 and 30% Cu with [NO] = 1000 ppm in He with 5% of  $O_2$ .

The influence of the type of structured material (melamine foam or cordierite monolith) used to support the catalysts is shown in Figure 8.



**Figure 8.** NO concentration in the presence of MF and CM with [NO] = 1000 ppm in He with 5% of  $O_2$ .

The NO reduction starts at 175 °C over the catalyst supported on CM, while using MF as support, the catalytic activity begins at about 225 °C. The best performance of the 2CM\_U\_10Cu sample is verified up to 325 °C, as the two materials reach the same conversion at that temperature. Although the results seem more attractive in relation to the catalyst structured with melamine foam, further studies on the characterization and other parameters of the NO reduction reaction with the catalyst structured with cordierite monoliths would be needed to discuss its catalytic performance [39].

#### 2.2.4. Stability Assay

A long-term test was carried out to verify the catalyst stability. Figure 9 shows the NO conversion profile obtained during 75 h at 300 °C for sample MF\_U\_30Cu.



Figure 9. NO concentration in a stability assay at 300 °C for 75 h.

Table 4 indicates the textural properties before and after the stability test.

Table 4. Textural properties of the MF\_U\_30Cu before and after the stability assay.

	m <sub>MF/</sub> g	$S_{\rm BET}/{ m m^2~g^{-1}}$	$S_{ m meso}/ m m^2~g^{-1}$	$V_{ m micro}/ m cm^3~g^{-1}$	$V_{\rm p\ p/po\ =\ 0.95}/{\rm cm^3\ g^{-1}}$
Before reaction	3.05	471	48	0.18	0.22
After reaction	1.79	796	140	0.27	0.35

From the beginning of the experiment the sample showed 98% conversion at 300 °C and the catalyst deactivation started after 20 h of reaction. Between 20 and 40 h, the catalyst loses activity, reaching a level of approximately 50%, which remains constant for the remaining hours of the test. With the catalyst deactivation, the carbon material significantly lost its mass causing the textural properties change (surface areas and pore volume increased). These results indicate that the materials under study are stable and catalytically active over a long period of time.

#### 3. Materials and Methods

3.1. Materials Synthesis

Powder Metal Catalysts

Carbon xerogels (CX), introduced by Pekala in 1989 [40], are porous materials obtained by carbonization of an organic gel that occurs through the sol-gel polycondensation of organic monomers, such as resorcinol ( $C_6H_6O_2$ ) (Sigma-Aldrich, Darmstadt, Germany, 99%) and formaldehyde (CH<sub>2</sub>O) (Sigma-Aldrich, Darmstadt, Germany, 37% in H<sub>2</sub>O), using a solvent and a basic catalyst as a reaction promoter [40–42].

CX were prepared at room temperature with an initial pH of 5.3 through the sol-gel polycondensation [37]. Two nitrogen precursors were used during the synthesis process, melamine (M) (99% Fluka, Buchs, Switzerland) and urea (U) (VWR, 100%), to prepare the nitrogen-doped carbon xerogels (CX\_N). The CX heat treatment was carried under a N<sub>2</sub> flowrate of 100 cm<sup>3</sup> min<sup>-1</sup> through three temperature increments at a heating rate of  $2 \degree C \min^{-1}$ . The plateaus were 200, 300 and 900 °C for 2, 1 and 2 h, respectively. Transition metal-carbon xerogels (CX\_TM) were prepared by incipient impregnation using three

metallic precursors: iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) (Sigma-Aldrich, 98%), nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) (Sigma-Aldrich, Darmstadt, Germany, crystalline) and copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) (Sigma-Aldrich, Darmstadt, Germany, 99–104%). The amount of impregnated metal corresponds to 10% (wt.%) and the CX and CX\_N (pH = 5.3) previously prepared were used as support. The CX soaked in the metal precursor solution was left for 1.5 h in an ultrasonic bath. Finally, the sample was placed in the oven for 24 h. The thermal treatment of CX\_TM was carried out under a flowrate of N<sub>2</sub> and H<sub>2</sub> of 100 cm<sup>3</sup> min<sup>-1</sup> at a heating rate of 10 °C min<sup>-1</sup>. The iron and nickel impregnated CX were heated from room temperature to 400 °C and the copper impregnated CX up to 300 °C under the flowrate of N<sub>2</sub>. After reaching the required temperature, the N<sub>2</sub> flowrate was maintained for 1 h. Then the sample was reduced in H<sub>2</sub> for 3 h.

Melamine foams (MF) (Basotect, BASF, Bucharest, Romania) and cordierite monoliths (CM) (Corning, Sigma-Aldrich, Darmstadt, Germany) were used as a template of the structured catalyst. Initially, MF/CM were cut with a diameter of 2 cm of and 4 cm of height. The supports were immersed in CX solutions with pH = 5.3 for 2 min and then placed in the oven for 3 days at 85 °C. After the drying period in the oven, the materials were heat treated in the same way as the CX. To carry out the metal impregnation on the supports, the necessary mass of copper nitrate corresponding to 10, 20 and 30% (wt.%) of the metal was determined. The samples were immersed in the corresponding solutions and left to stir for 24 h. Oven drying and heat treatment are equivalent to those described for CX\_TM. To name the samples, the following order was followed: support (CX, MF or CM), nitrogen precursor (M or U) and amount (10, 20 or 30) of impregnated metal (Fe, Ni or Cu) (Ex: MF\_U\_10Cu).

#### 3.2. Characterization Techniques

Nitrogen adsorption-desorption equilibrium isotherms at -196 °C were performed in a Quantachrome Instruments equipment (Quantachrome Instruments, Boynton Beach, USA) to determine the textural properties of the synthesized materials. The BET method was applied to calculate the specific surface area ( $S_{\text{BET}}$ ), whereas the specific surface area of mesopores ( $S_{\text{meso}}$ ) and the specific micropore volume ( $V_{\text{micro}}$ ) were determined by the t-method.

The nitrogen content of the prepared materials was determined by elemental analysis (EA) in the CHNS vario MICRO cube analyzer (Kalkar, Germany).

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES), using the ICPE-9000 spectrometer (Shimadzu, Auckland, New Zealand), allowed determining the copper concentration present in MF.

A Thermo Scientific Escalab 250Xi (Porto, Portugal) spectrometer was used for X-ray photoelectron spectroscopy (XPS), using a monochrome and microfocused Al K $\alpha$  X-ray source. The fit of the spectra peaks was performed using the Thermo Fisher Scientific (Porto, Portugal) Avantage program.

Thermogravimetric analysis (TGA) was performed on the Netzsch STA 409 PC/PG (Selb, Germany) equipment using a dynamic method. The samples were heated to 900 °C using an air flowrate of 20 cm<sup>3</sup> min<sup>-1</sup>.

The morphology of the materials and the adhesion of carbon to MF was observed by scanning electron microscopy (SEM) on a Quanta 650 FEG microscope (FEI, Marietta, GA, USA).

#### 3.3. Catalytic Tests

The tests using the powder materials were carried out in a U-shaped fixed bed microreactor with a diameter of 0.7 cm, where 200 mg of catalyst with a particle size between 200–500  $\mu$ m was placed. In the catalytic tests using the structured catalysts, a U-shaped reactor with a diameter of 2.6 cm was used. The reduction of NO was carried out under a total flow rate of 100 cm<sup>3</sup> min<sup>-1</sup> with a concentration of 1000 ppm NO in He and 5% O<sub>2</sub> (Figure A3) in the temperature range of 125 to 350 °C with a heating ramp of 3 °C min<sup>-1</sup>.

The conversion of NO ( $x_{NO}$ ) was calculated according to Equation (3).

$$x_{\rm NO} = \left(1 - \frac{c_{\rm NO}}{c_{\rm NO_0}}\right) \times 100 \tag{3}$$

# 4. Conclusions

Nitrogen oxides are considered one of the pollutants that cause the greatest concern in terms of atmospheric contamination. In this sense, the main objective of this work was the synthesis and characterization of structured carbon catalysts, introducing metals and nitrogen groups, catalytically active in the reduction of NO to contribute to the reduction of its emissions.

In the NO reduction tests performed with CX, the presence of transition metals in the structure was essential for catalytic activity and the introduction of nitrogenous groups in the CX structure, using melamine as a precursor, enhanced the catalytic results. The MF samples with urea showed the best performance in reducing NO and simultaneously had the highest content of copper in their structure, so it appears that the incorporation/concentration of copper in the materials is a determining factor in the catalytic reduction of NO into  $N_2$ . Cordierite monoliths are a promising support alternative for the catalytic activity to be favored at low temperatures.

Although CX, MF and CM, have high conversions in the catalytic reduction of NO to  $N_2$  at temperatures between 300 and 350 °C, structured catalysts represent a preferable alternative to powder catalysts because they have better thermal stability and lower pressure drop. This advantage is fundamental for applications in industrial processes.

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**Figure A1.** NO concentration in blank tests with [NO] = 1000 ppm in He with 5% of O<sub>2</sub>.

The NO conversion profile shown in Figure A1 is similar in the two reactors, where the decreasing peaks between 50 and 75 °C result of the experimental setup configuration, namely the passage through the NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer of the dead volume of air present in the reactors and piping at the beginning of the reaction. The presence of O<sub>2</sub> promotes the reduction of NO and, therefore, a lower  $c_{NO}/c_{NO_0}$  plateau is observed compared to the initial concentration of NO, 1000 ppm. The homogeneous conversion of NO differs only 1% between the two tests, being 14% for the 0.7 cm reactor and 13% for the 2.6 cm reactor.

To understand the oscillations of the concentration along the studied reactions, two tests were carried out changing the initial temperature of the reaction, 25 and 50 °C, using the CX\_Cu catalyst (Figure A2).



**Figure A2.** NO concentration in the presence of CX\_Cu with initial reaction temperature of 25 and  $50 \,^{\circ}$ C and [NO] = 1000 ppm in He with 5% of O<sub>2</sub>.

The depressions observed between 30 and 100 °C suggest that NO is first adsorbed on the surface and then desorbed with increasing temperature, causing an increase in NO concentration above 1000 ppm [43].

From Figure A2, it can be seen that in the reaction starting at 25  $^{\circ}$ C, there is greater adsorption of NO in the initial phase than in the test started at 50  $^{\circ}$ C. In the desorption part, exactly the same is verified, with a greater amount of NO desorbed in the test carried

out at the lower temperature. However, the amount of adsorbed and desorbed NO at the beginning of the reaction does not interfere with the catalytic results obtained at higher temperatures, since from 300  $^{\circ}$ C the two curves overlap and give the same NO conversion value.

Between 150 and 225  $^{\circ}$ C there is a slight decrease followed by an increase in the concentration of NO; this change can be justified based on the oxidation states of copper, since in the experiments with the other metals this behavior was not observed [44].

In Figure A3, the conversion curves of NO and  $NO_2$  obtained in the catalytic tests of NO reduction are represented to evaluate which would be the reaction products.



**Figure A3.** NO and NO<sub>2</sub> concentrations in the presence of CX and CX\_N with and without metals with [NO] = 1000 ppm in He with 5% of O<sub>2</sub>.

As insignificant amounts of  $NO_2$  (grey lines) were detected as reaction products in all temperature ranges, under these experimental conditions, it is assumed that  $N_2$  is the only observed reaction product.

The presence of  $O_2$  in the NO current causes the amount of reduced NO to increase, but the ideal amount of oxygen is not known [34]. Therefore, the tests described in Figure A4 were obtained to verify if the increase in the concentration of  $O_2$  in the gas stream influenced the performance of the catalysts in reducing NO. The behavior of MF\_U\_10Cu was evaluated in the presence of 5, 10 and 20%  $O_2$ .



**Figure A4.** NO concentration in sample MF\_U\_10Cu with [NO] = 1000 ppm in He with 5, 10 and 20% of  $O_2$ .

Table A1 presents the catalyst mass lost during the reaction with MF\_U\_10Cu in the presence of 5, 10 and 20% of O<sub>2</sub>.

**Table A1.** Catalyst mass lost during the reaction in the presence of MF\_U\_10Cu samples under 5, 10 and 20% O<sub>2</sub>.

Sample	m <sub>lost_in_reaction</sub> /%		
MF_U_10Cu_5_O <sub>2</sub>	1.6		
MF_U_10Cu_10_O <sub>2</sub>	4.2		
MF_U_10Cu_20_O <sub>2</sub>	7.2		

Analyzing the results of Figure A4, between 200 and 250 °C the reduction of NO increases with the increase in the concentration of  $O_2$  used; however, for temperatures above 250 °C the increase in the concentration of  $O_2$  is significant when it increases from 5 to 10% but increasing this parameter beyond 10% has no positive influence on the NO conversion. The maximum conversion of NO obtained for 5 and 10% is 95% at a temperature of 350 and 338 °C, respectively. The mass of the MF samples lost during the reaction increases with the increase in the concentration of  $O_2$  in the gas stream due to the gasification of the sample, which shows that the samples are less stable in the presence of a greater amount of  $O_2$ . Although the maximum conversion temperature in the MF\_U\_10Cu\_10\_O<sub>2</sub> test is slightly lower than in the MF\_U\_10Cu\_5\_O<sub>2</sub> test, the results obtained at 5% O<sub>2</sub> are also quite attractive and the stability of the samples is higher, which makes the increase of the oxygen concentration in the NO stream unfavorable.

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