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FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

DEVELOPMENT OF N-DOPED CARBON CATALYSTS FOR SIMULTANEOUS NO AND CO REDUCTION

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DISSERTAÇÃO DE MESTRADO APRESENTADA
À FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO EM
ENGENHARIA QUÍMICA

Master's in chemical engineering

Development of N-doped carbon catalysts for simultaneous NO and CO reduction

Master dissertation

of

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Developed within the course of dissertation

held in

International Iberian Nanotechnology Laboratory, Laboratory of Separation and Reaction Engineering and Laboratory of Separation and Reaction Engineering

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October 2020

Acknowledgement

I would like to thank all the people who contributed to this dissertation.

Firstly, to Dr. Salomé Soares, whose guidance and constant assistance was paramount to this work, even when distance would be a limitation.

Secondly, to Dr. Juliana Sousa who would tirelessly provide supervision and support in all aspects of the work, on and off the lab.

To Dr. João Restivo for his immense assistance throughout the lab work.

To Prof. Fernando Pereira, to his cooperation both to this work and to the LRSE-LCM.

To Dr. Yury Kolen'ko, for his friendliness, which surely made my stay at the INL ever more enjoyable.

To Patrícia Ramalho for all the help to solve all the technical challenges that surfaced during my stay at the LRSE-LCM.

I would also like to thank all the people at LRSE-LCM and at INL for all the help and support provided. Your knowledge proved invaluable to this work.

To my family, for their unwavering support before and during the writing of this work.

To all my friends, old and new ones for their presence in all my university years. You all have made an irreplaceable impact on my life. I hope I made your life as special to you as you made mine.

This work was financially supported by: Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC).

Abstract

Pollutant emissions have been a looming problem that has led to many environmental impacts which have bled into human life. Many compounds, among them nitric oxides, are being released into the atmosphere at increasing rates as civilisations became more industrialised. Nitric oxide has become a problem as it is a significant contributor to a wide range of consequences that negatively impact the environment. Despite all the efforts carried out until today, the currently available techniques have revealed to be insufficient to remove nitric oxide from streams. To improve the current technologies, this dissertation aims to study the reduction of nitric oxide (NO) using nitrogen-doped carbon materials as catalysts in the presence of oxygen and/or carbon monoxide.

For this end, structured catalysts were prepared by the polycondensation of resorcinol with formaldehyde in which a melamine foam was dipped. These materials were characterised resorting to thermogravimetric analysis, SEM imaging, nitrogen adsorption isotherms at -196 ºC and elemental analysis. To evaluate the catalytic performance of the materials reactions of NO reduction were carried out in a fixed bed reactor, using different experimental conditions, more notably the inlet condition. More specifically, in order to have a deeper understanding of the influence of the operation conditions, assays were carried out in the presence of carbon monoxide as well as with (or without) oxygen. The planning of the catalytic assays was performed according to the Design of Experiments methodology, which allowed for more conclusive results despite the time constraints related to the pandemic situation.

From the characterisation results, it was concluded that all the prepared samples had a low surface area and good thermal stability in a helium atmosphere. The elemental analysis showed that the different synthesis variables have a sizeable impact on the samples composition.

Despite the high content of nitrogen groups present in the samples, the low surface area values committed its catalytic performance. Nevertheless, the N-doped structured carbon materials revealed to be promising catalysts for NO reduction when compared to other carbon materials. Nitric oxide conversions between 15 and 29% were achieved with the developed materials. The synthesis variables that had the most impact in the conversion were pH, nitrogen precursor, soaking time and exposure to compressed air. Notwithstanding, the surfactant has also shown some level of impact on the conversion. Moreover, it was also observed that these variables' effects would interact with other variables, meaning that their combined effect is as important as their isolated effects.

Keywords (theme): N-doped carbon material, catalysts, nitric oxide, reduction,

Resumo

As emissões poluentes têm sido um problema emergente que levou a vários impactos ambientais que por sua vez atingiram a vida humana. Há muitos compostos, entre eles os óxidos nítricos, que são libertados para a atmosfera a um ritmo crescente à medida que as civilizações se tornam cada vez mais industrializadas. O óxido nítrico tornou-se problemático uma vez que contribui para um conjunto de uma gama de consequências negativas que afetam o ambiente. Apesar de todos os esforços feitos até hoje, as técnicas hoje disponíveis mostraram-se insuficientes para remover o óxido nítrico dos efluentes. Para melhorar as tecnologias atuais, esta dissertação tem como objetivo estudar a redução do óxido nítrico (NO) através do uso de materiais de carbono dopados com grupos azotados como catalisadores na presença de oxigénio e/ou monóxido de carbono.

Para este fim, catalisadores foram preparados através da policondensação de resorcinol com formaldeído no qual a espuma de formaldeído foi mergulhada. Estes materiais foram caracterizados com recurso à análise termogravimétrica, imagiologia SEM, isotérmicas a -196 ^{o}C e análise elementar. Para avaliar a performance catalítica dos materiais, as reações de redução de NO foram conduzidas num reator de leito fixo, com diferentes condições experimentais, mais notavelmente as condições de alimentação. Mais especificamente, para obter uma maior compreensão da influência das condições operatórias, ensaios foram feitos na presença de monóxido de carbono e também com (ou sem) oxigénio. O planeamento dos ensaios catalíticos foi feito de acordo com a metodologia de Projeção de experiências, que permitiu obter resultados mais conclusivos apesar das restrições de tempo.

A partir dos resultados da caracterização, concluiu-se que todas as amostras preparadas tinham uma área superficial baixa e uma boa estabilidade térmica numa atmosfera de hélio. A análise elementar mostrou que as diferentes variáveis de síntese têm um efeito considerável nas composições das amostras.

Apesar da elevada quantidade de grupos de azoto nas amostras, os baixos valores de área de superfície comprometeram o seu desempenho catalítico. No entanto, os materiais de carbono estruturados dopados com grupos azotados mostraram-se promissores para a redução do NO quando comparados com outros materiais de carbono. As conversões de óxido nítrico obtidas com os materiais desenvolvidos variaram entre 15 e 29%. As variáveis de síntese que tiveram o maior impacto na conversão foram o pH, o precursor de azoto, o tempo de imersão e a exposição a ar comprimido. No entanto, o tensioativo também revelou ter algum impacto sobre a conversão. Adicionalmente, foi também observado que os efeitos das variáveis também interagem com outras variáveis, pelo que o seu efeito combinado é tão importante quanto os seus efeitos isolados.

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source

Sign and date

Arnaldo Filipe Gouveia Espírito Santo Neto

21-09-2020

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Notation and Glossary

C_{NO}	Nitric oxide concentration (ppm)
C_{NO0}	Initial nitric oxide concentration (ppm)
X	Conversion
T	Temperature (ºC)
h	Planck constant (J*s)
v	Photon frequency (Hz)
X_{max}	Maximum conversion
λ	Wavelength (nm)

List of Acronyms

ASC	Ammonia-slip catalysts
CNT	Carbon nanotubes
De-NO_x	Removal of nitric oxides
EA	Elemental Analysis
NO_x	Nitric oxides
SCR	Selective catalytic reduction
SEM	Scanning Electron Microscopy
SOF	Soluble organic fraction
SO_x	Sulphur oxides
TGA	Thermogravimetric analysis
TWC	Three-way catalytic converter
X_{max} NO	Maximum nitric oxide conversion
XPS	X-ray photoelectron spectroscopy

1 Introduction

1.1 Framing and presentation of the work

Over the past decades, industrialisation has seen steady growth, which has been accompanied by an increase in air pollution. With time, this increase eventually reached pollution levels where its effects had become noticeable. More specifically, the effects caused by nitric oxide had contributed towards smog, an increase of tropospheric ozone concentration as well as the formation of other harmful compounds.

These emission consequences led people to take more conscious action towards pollution, thus leading to the development of different strategies to reduce these emissions. Even though significant progress has been made, the solutions developed so far have been insufficient to overpower the excessive nitric oxide emissions due to the limitations they currently possess.

With this problem in mind, this work will focus on the development of carbon-based catalysts for the reduction of nitric oxide into molecular nitrogen; therefore, reducing the number of pollutants effectively reaching the atmosphere. To accomplish this aim experiments of NO reduction over the developed catalyst were carried out under different operating conditions and the catalysts were characterised by different techniques: scanning electron microscopy, N_2 adsorption isotherms at -196 ºC, thermogravimetric analysis and element analysis.

1.2 Presentation of the company

The International Iberian Nanotechnology Laboratory (INL), founded in 2005 by the Portuguese and Spanish Government, is located in Braga and it is a multidisciplinary research compound founded by the governments of Portugal and Spain. INL focuses on using nanotechnology to respond to the many challenge's society is being presented today. The centre provides a high-tech research environment to address major challenges of nanotechnologies, in four main areas: Health, Safety in Environmental and Food control, Renewable Energy, Information and Communication Technologies. The INL building was designed for a total staff of 400 people, including Principal Investigators (PIs), staff researchers, visitors, research fellows, PhD students, support engineers and administrative support staff. Currently, there are 401 people working at INL, being 306 people scientists.

1.3 Contribution of the author to the work

The author has prepared all the catalysts used in this work at the INL facilities and have carried out all the catalytic tests at the LRSE-LCM. Additionally, the author has carried out the characterisations of all the samples except for the SEM analysis.

1.4 Organization of the thesis

This dissertation is organised in 6 chapters. Chapter 1 will address the overall framing of the work developed as well as briefly introducing the institutions where it is being developed.

Chapter 2 will show the background information required for this work as well as how the current socio-political climate has prompted the need the research questions addressed.

Chapter 3 will narrow down on the materials and methods utilised over the course of this work.

The characterisation and catalytic results are shown in chapter 4 as well as the discussion of the results obtained.

Chapter 6 will assess the work done during the dissertation.

Lastly, the appendix will show relevant data to chapter 4.

2 Context and State of the art

2.1 Pollution

The Merriam-Webster Dictionary defines pollution as the action of polluting, especially by environmental contamination with man-made waste [1]. Such waste is presented in various forms, including flue gases, liquid effluents, or solid materials (either in the macro- or microscopic scale) and thus the different types of pollution are categorised by their origin, physical state, or by a particular property (e.g.: dimension). What is more, their continual release over the last decades has dealt substantial damage to the environment. This damage could be mitigated and reversed if pollution was curbed, which has not happened yet despite the collective effort made by several organisations, governments, and individuals. This is explained by the fact that firstly, some companies – or entire sectors – have failed to comply with European guidelines, which is partly owed to the struggle to find appropriate methods to regulate the applications of these guidelines [2]. Secondly, some countries have not adopted environmentally friendly policies. And lastly, it has reached the point where nations have withdrawn from worldwide agreements [3]. Nevertheless, some governments actively try to conform to these guidelines, despite still failing to meet the required goals. As such, the enumerated reasons have obviated that pollution must be tackled because failing to do so could potentially result in irreversible damage to various ecosystems, ultimately jeopardising human society's current way of life. To avoid that, several measures have been created [4]. Additionally, the reluctance some nations has shown towards joining global agreements (one example would be Iran, USA, and Turkey opting to stay out of the Paris Agreement) also represents a major hindrance to the effectiveness to any employed measures. And finally, countries failing to achieve the emission goals set need to receive external help as, as it stands, they do not have the resources and/or knowledge to reach such emission targets. Nevertheless, other countries have found success in achieving such targets. For instance, Portugal's target for nitric oxide emission from 1990 to 2020 was a 27% reduction as per the Gothenburg targets and it has obtained a 31% reduction [5].

Having mentioned emission targets, it becomes necessary to mention air pollution due to its contribution to ozone depletion, acid rain, biodiversity, and climate change. All these phenomena contribute to several calamities (Figure 2-1) such as droughts, floods, and other meteorological phenomena, which in turn have led to the displacement of millions of people and even hundreds of deaths.

Figure 2-1 – *Depiction of the consequences of climate change [6]*

2.1.1 Atmospheric Pollution

Air pollution is defined as the presence of airborne substances in enough quantities to cause adverse effects in living beings and on exposed materials. In the air, it is possible to find several pollutants such as carbon dioxide, nitrogen oxides (NO_x), ammonia, sulphur oxides, non-methane volatile compounds, and fine particulate matter [7]. The air pollution is primarily generated by industrial activity, transportation, and energy production [8-10].

One of the most prominent air pollutants, nitrogen oxides (NO_x), are compounds formed by a combination of oxygen and nitrogen. There are different types of NO_x compounds – characterised by the various combinations of nitrogen and oxygen –, such as NO, NO_2, NO_3, N_2O_5, N_2O, and N_2O_4. Among these, NO and NO_2 are the most commonly released in flue gases, comprising 90 to 95% of the total NO_x emissions [11].

2.1.2 Nitric oxide emissions

Anthropogenic sources, such as motorised transportation and industrial activity [8-10] are the main source of nitric oxide emissions. In fact, only 10% of them are originated by biogenic sources. Spite of their continuous emission from several sources, there has been a downward trend in NO_x emissions in the European Union (EU), as shown in Figure 2-2. This can be explained

by the emission reduction policies placed by the EU and other international agreements – more notably the Paris Agreement signed in 22nd of April 2016 - that have been made. Notably, the Paris Agreement's emission reduction policies impact was visible on the global trend on emissions as soon as 2017 [12]. Additionally, several technological advancements have resulted in a decrease in emissions from vehicles and the energy sector. On top of that, the increase in public awareness towards environmental issues has had a strong influence on the everyday lives of many citizens, which in turn has led them to acquire a more ecologically friendly attitude.

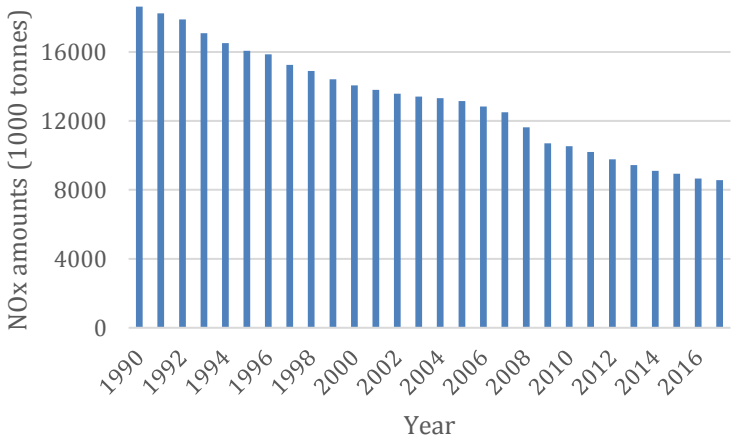

Figure 2-2 – *Evolution of EU NO_x emissions [7].*

Similar to other countries, Portugal nitric oxide emissions come mostly from the transport sector [13]. Moreover, this country has taken part in the Paris Agreement and has attempted to adhere to EU guidelines, and as previously mentioned, recent results have shown it has managed to comply with the 2020 objective, i.e. an emission reduction in 27% [5]. However, several countries, including Spain, Norway and Austria, were not able to reduce their nitric oxide emissions.

At an European level, EU has set several guidelines to directly or indirectly reduce the emissions of nitrogen oxide [14]. These imposed guidelines include air quality standards for nitrogen oxides family. More precisely, the nitrogen dioxide air quality standards dictate that a maximum of 200 $\mu g/m^3$ (0.1 $\mu g /m^3$ in the US) per hour [15] can be released into the atmosphere.

2.1.3 Nitric oxide impact

Despite being targeted by strict regulations, nitric oxide's current emission levels are still high enough to have negative effects on all life on Earth. The presence of high concentrations of nitric oxide concentrations has a destructive influence both in the environment and in human health.

Nitric oxide emissions significantly affect the environment in several ways. The emission of this gas contributes to the ozone layer destruction, as demonstrated by Equation 2-1 through Equation 2-3 [16].

$$O_3 + hv \rightarrow O + O_2$$ *Equation 2-1*

$$O + NO_2 \rightarrow O_2 + NO$$ *Equation 2-2*

$$O_3 + NO \rightarrow O_2 + NO_2$$ *Equation 2-3*

Other impacts caused by NO include its role as a precursor to the formation of nitrogen dioxide (as demonstrated in Equation 2-1) as well as its contribution to the formation of acid rain and tropospheric ozone [17].

Concerning to the formation of tropospheric ozone, its first step is the photodissociation of NO_2 into nitric oxide and oxygen.

$$NO_2 + hv(\lambda < 430\ mn) \rightarrow NO + O_2$$ *Equation 2-4*

Afterwards, the oxygen formed will react with molecular oxygen, thus giving rise to tropospheric ozone [18].

$$O + O_2 \rightarrow O_3$$ *Equation 2-5*

As for the origin of acid rain, shown in Equation 2-6, nitrogen dioxide interacts with a hydroxyl radical, thus forming nitric acid, which results in the acidification of rain.

$$OH + NO_2 \rightarrow HNO_3$$ *Equation 2-6*

Current emission levels of nitric oxide are destructive not only to the environment but also to human health as the NO interacts with transition metals or oxygen-containing proteins, in addition to its ability to traverse cell walls and to induce oxidative stress. Consequently, it can be responsible for cardiovascular, respiratory, and pulmonary conditions. On the economic side of the issue, these health issues lead to more sick leaves, which represents a hindrance to productivity, thus making this public health issue a problem to industries as well. Additionally, as stated above these emissions can lead to the formation of tropospheric ozone, which in turn has been reported to be detrimental to human health [19].

2.1.4 Removal strategy

The following sections will focus on the various methods that have been utilised alongside policies and legislation to mitigate this issue. The approaches to be mentioned are both the robust pre-existing technology that has been widespread in various industries as well as the

research that has been done to find alternatives that can to improve upon currently existing technology.

Within the widespread technology, numerous removal strategies have been developed. Among them, the next sections will describe the most use. These removal strategies can be subdivided into two types, according to the undertaken approach: primary and secondary measures.

2.1.4.1 Primary measures

Primary measures are defined as the analysis of the procedural variables and the factors that determine the formation of nitric oxides, in order to prevent their formation. This analysis has led to improvements in furnaces, burners, among other technologies. Among them, the fluidised bed combustion and air staging techniques are the most used.

2.1.4.1.1 Fluidised bed combustion

Fluidised bed combustion is a common process in coal burning [20]. As the name implies, during this process's operation coal is fed into the reactor's bed, which was previously heated until the desired temperature. A lab-scale assembly is represented in Figure 2-3.

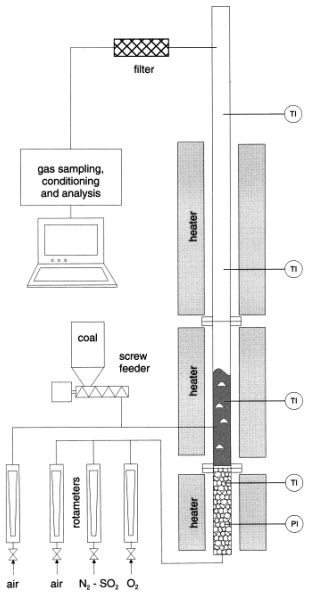

Figure 2-3 – *Lab-scale assembly of the fluidised bed combustion of coal [20]*

This solution has the advantage of operating at lower temperatures (typical operating temperatures are between 750 - 927 ºC), which has led to the formation of smaller amounts of nitric oxide (and other nitrogen oxides) [20]. This smaller NO formation occurs because nitric

oxide requires higher temperatures to be formed. Aside from temperature, NO emission can also be mitigated by fine-tuning fuel type, excess air, limestone feed, pressure, air staging, and boiler load [21]. However, coal is gradually being phased out. That, in conjunction with its incompatibility with the vehicle industry, makes fluidised bed combustion a very unappealing solution to tackle NO and NO_2 emissions in the long run.

2.1.4.1.2 Air staging

Air staging is characterised by the separation of the air required in combustion in several streams, which are then fed into the required equipment and is it often applied in furnaces, coal, oil boilers, and vehicles. This separation of air streams results in the mitigation of the formation of nitric oxides in virtue of the reduction of the availability of O_2, O, and OH, which promotes the formation of nitric oxides [22].

The operation occurs as it is illustrated in Figure 2-4. The air stream is separated and fed into different points of the boiler (in opposition to feeding it in just one stage), which causes the formation of pockets in the primary zone – which are responsible for the lower temperatures in this zone – but also the formation of fuel-rich zones[23].

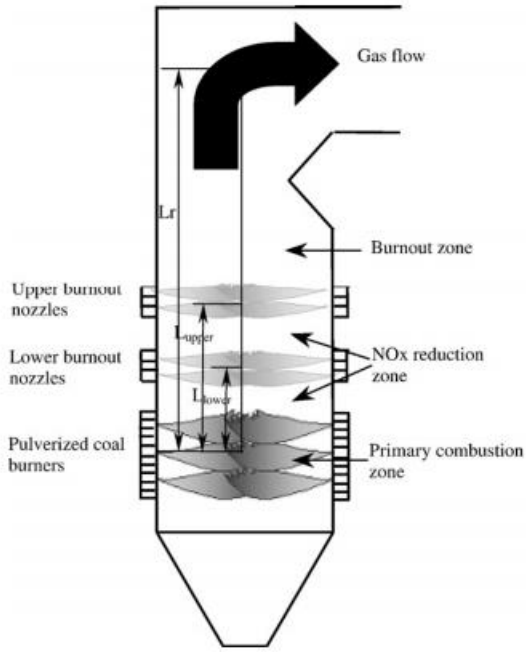

Figure 2-4 - *Air staged combustion system [24]*

Additionally, this method also promotes lower temperatures in the primary combustion, which further reduces the amount of NO_x generated [23]. The commonly reported temperatures are

close to 850 °C [25] in furnaces and within the 850 to 930 °C range for boilers [26]. With this method, it is possible to achieve a reduction of the nitric oxide emissions by 50%. However, this reduction occurs in fuel-rich conditions, which promote the formation and subsequent emissions of hydrogen cyanide [22].

2.1.4.2 Secondary measures

Along with primary measures, a popular set of approaches to mitigate the NO emissions are the secondary measures, such as emission control techniques. These measures allow reducing the nitric oxide compounds that are already formed in the combustion process. In the next sub-sections will be described the secondary measures more promising to reduce the NO_x emissions to the environment.

2.1.4.2.1 Three-way catalytic converters (TWC)

Three-way catalytic converters are a technology that involves the use of metals, placed on the surface of honeycomb-shaped support to convert the exhaust gases into less harmful compounds, as shown in Figure 2-5. The metals more commonly used for the construction of this type of catalysts are noble metals (platinum, palladium and rhodium).

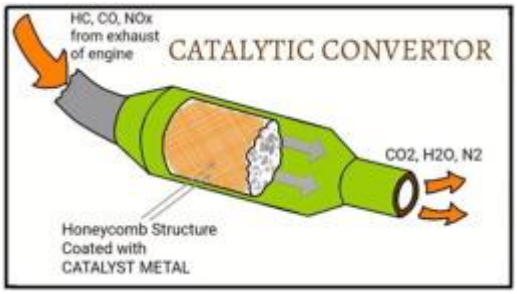

Figure 2-5 – *Catalytic converter scheme [27]*

Even though three-way catalytic converters are an effective solution as a secondary approach to internal combustion engines, diesel car exhausts contain soot (dry carbon particles), liquid fuel, and SOF (soluble organic fraction – liquid fuel and oil mixture) and significant amounts of sulphur dioxide, which would be converted to sulphuric acid over oxidation catalysts, which is a harmful product. Because of these compounds, catalytic converters are not suitable for diesel cars [28].

2.1.4.2.2 Selective catalytic reduction (SCR)

The reduction of nitric oxide requires relatively high temperatures, which can become an obstacle due to the equipment or resources needed to achieve them. To decrease the reaction temperature, some reductant species can be used, such as ammonia, hydrogen and carbon monoxide.

Among these compounds, ammonia is a rather popular compound for selective catalytic reduction. This technology involves the use of a honeycomb structure as a support for the catalyst, as shown in Figure 2-6. This alternative is a popular method for the catalytic reduction of nitric oxide [29, 30] in diesel engine vehicles and electric plants. Commercially, the most popular metal for this type of catalysis is the vanadium-titanium based SCR catalysts (V_2O_5-WO_3/TiO_2) [31], although they still require the presence of ammonia.

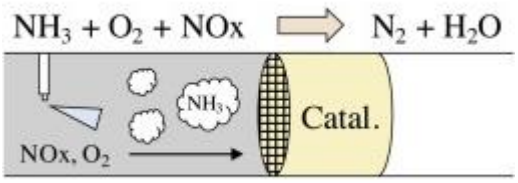

Figure 2-6 – *SCR system [32]*

In this system, similarly to three-way catalytic converters, the exhaust gases are introduced in the device chamber. Then, the ammonia source, which is usually urea, is also introduced in the chamber. The conversion of urea into ammonia is described below in Equation 2-7 and Equation 2-8.

$$(NH_2)_2CO \rightarrow NH_3 + HNCO\ (thermolysis) \qquad \textit{Equation 2-7}$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \qquad \textit{Equation 2-8}$$

After this conversion, the newly formed ammonia and the exhaust gases then flow into the catalyst, where the catalytic reduction of nitric oxide occurs. This catalytic reduction of NO is described by Equation 2-9$NH_3 + NO \rightarrow N_2 + H_2O$ Equation 2-9:

$$NH_3 + NO \rightarrow N_2 + H_2O \qquad \textit{Equation 2-9}$$

In Figure 2-7, it is possible to observe the interactions between the catalyst, the reactants, and all the intermediary species.

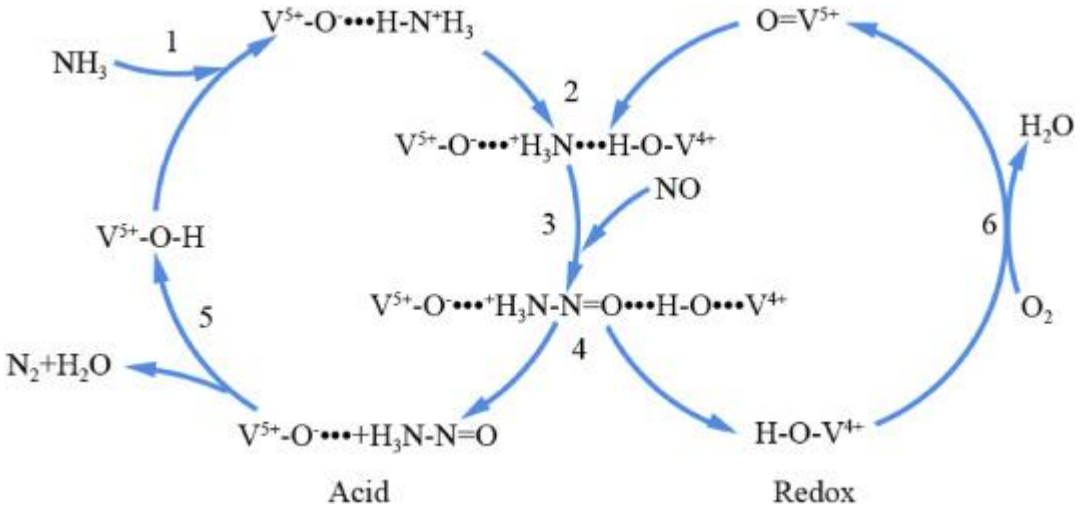

Figure 2-7 – *SCR mechanism of the removal of nitrogen oxides from gases [31]*

This catalytic process has shown to be able to reduce nitric oxide at temperatures as low as 200°C reaching conversions above 90% [33] even though it is plagued by ammonia slip [34] – unreacted ammonia in the outlet exhaust gases. Admittedly, this issue can be mitigated by ammonia slip catalysts (ASC). However, this sort of catalysts often time require expensive metals. Besides, their performance is affected by the presence of sulphur and sulphates – which are often present in diesel engine exhaust gases [35].

Beyond ammonia, other compounds can be used as reducing agents for SCR. One popular alternative is molecular hydrogen. The use of hydrogen was due to its occurrence in exhaust gases that were output from combustion, which meant no outside addition of hydrogen would have been required for the reaction happen. The reaction occurrence, as depicted in Equation 2-10, is characterised by the dissociation of nitric oxide into oxygen and nitrogen. From there, the oxygen will adsorb into the catalyst, where it will react with the hydrogen, thus originating water. It should be added that the catalysts used in this reaction are generally noble metals, such as gold, platinum, palladium, and osmium [36].

$$2\,NO \rightarrow N_2 + O_2 \overset{H_2}{*\rightarrow} H_2O \qquad \textit{Equation 2-10}$$

However, this reaction leads to side-products. As it is observed in Equation 2-11, the reduction reaction can also originate ammonia [36].

$$NO + \frac{1}{2}H_2 \leftrightarrow H_2O + NH_3 \qquad \textit{Equation 2-11}$$

Regarding operating temperature ranges, 90% of NO conversion was reported within the 195-414 °C range by using a vanadium-based catalyst (more specifically V-Ce-Ni/TiO_2-HP). This same catalyst was able to achieve 100% conversions at 230-250 °C [33]. The formation of ammonia (Equation 2.1) as a sub-product is one of the disadvantages of this method.

2.1.4.2.3 Catalytic reduction of NO by CO

As an alternative to hydrogen, the reduction of nitric oxide can be carried out by carbon monoxide. This compound is a pollutant gas, present in exhaust gases due to incomplete combustion of hydrocarbons. The catalytic reduction of NO by CO can simultaneously remove two pollutants from the exhaust gases.

Carbon monoxide reacts with NO, forming nitrogen and dioxide carbon in Equation 2-12.

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad \textit{Equation 2-12}$$

Generally, this reaction is catalysed by precious metals, being rhodium the most usual choice.

The reaction mechanism of catalytic reduction of NO by CO in the presence of metal catalysts has the following step: NO and CO adsorption, NO dissociation, N_2O formation and dissociation, CO_2 formation, and lastly N_2 formation as shown in Equation 2-8.

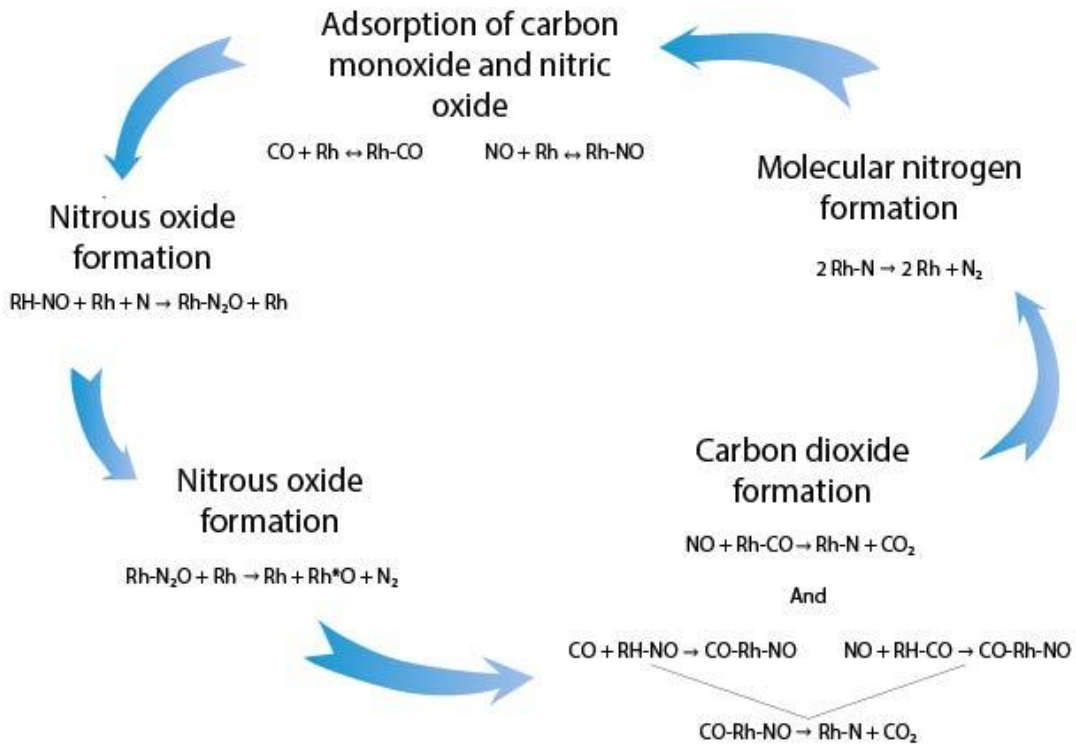

Figure 2-8 - *Catalytic reduction mechanism of nitric oxide in the presence of rhodium catalyst [37]*

Despite its effectiveness in the reduction reaction, rhodium catalysts are one of the most expensive metals commercially utilised to carry out this reaction – rhodium can cost as much

234 USD per gram. Therefore, cheaper and effective alternatives to rhodium are required, thus leading to the research of the use of alternative metals.

The catalytic reduction of NO with CO can be perform using transition metal oxides, such as copper and iron (the iron can even be waste iron [38]), and they have shown performances comparable to rhodium [39]. These metals can be used in conjunction with metal oxides such as titanium, where their interaction improves the selectivity towards the formation of molecular nitrogen [40]. These catalysts could even retain their catalytic activity after being exposed to 350 h of leaded exhaust fumes [41]. The copper-titanium supported catalysts [42] have also shown great activity and selectivity regarding the molecular nitrogen formation.

Despite the promising catalytic activity obtained with the metal oxides, its stability is still far away from the obtained when the catalyst is a noble metal. However, it should be mentioned that the precious metal catalysts have been reported to have better stability when exposed to atmospheres containing molecular oxygen, water and sulphur dioxide [43], which could be a common occurrence during operation in a real-world setting. That said, even though the alternative metals have shown promising results, they still need further means to become as stable as noble metals.

In the sections above, was discussed the different technologies available to treat nitric oxide emissions. Several factors have hampered the commercialization of these technologies, such as the need to use high reaction temperatures, the use of expensive metallic catalysts, or the formation of other harmful by-products.

In this work, it is intended to give alternatives that can overcome those shortcomings. Our proposal is to use metal-free catalysts like nitrogen-doped carbon materials as a catalyst in nitric oxide reduction.

2.1.4.2.4 Catalytic reduction of NO by CO with carbon materials

Carbon materials are widely used as catalyst supports [44], but their use as a catalyst is attracting a great deal of attention [45]. The major advantages of carbon materials as metal-free catalysts is the possibility of being effective in the NO removal in the presence of sulphur, oxygen and water vapour [46], they are relatively inexpensive and have significant activity at lower temperatures, thus constituting a promising potential alternative to traditional catalysts.

The reaction between the nitric oxide and carbon materials starts with the chemisorption of NO into the surface of the materials. Here, the nitrogen atom in the NO bonds with the nitrogen atom in the carbon material, as it is shown in Equation 2-13.

$$*N + NO \rightarrow *N - NO$$ *Equation 2-13*

Then, as per Equation 2-14, the oxygen atom from the nitric oxide also interacts with the carbon forming the *N-NO* intermediate.

$$* \mathrm{N} - \mathrm{NO} + * \rightarrow * \mathrm{N} - \mathrm{NO} *$$ Equation 2-14

Afterwards, this intermediate compound dissociates into adsorbed N_2 and adsorbed oxygen, as shown below. The oxygen atom will remain adsorbed, thus originating carbonyl groups.

$$* N - NO * \rightarrow * N_2 + * O$$ *Equation 2-15*

This is succeeded by the desorption of N_2 present [47], as shown in Equation 2-16.

$$* N_2 \rightarrow N_2 + *$$ *Equation 2-16*

Now, there one more pathway that must be addressed, which is the formation of nitrogen dioxide [36]. This pathway shows the difficulty of the direct conversion of nitric oxide into molecular nitrogen. Preferably, the reaction pathway often converts NO into an intermediary – nitrogen dioxide in this case that will be converted into nitrogen afterwards. This paves the way for other pathways instead of the ones mentioned above. In other words, pathways that may originate NO_2 are still viable as it can be converted into molecular nitrogen. This means that, even though the oxygen present in the inlet stream may oxidise the present nitric oxide, if the catalyst was chosen carefully, this oxidation, can become beneficial to the conversion and selectivity of the reaction.

2.1.4.2.5 Catalytic reduction of NO by CO over carbon materials in the presence of O_2

In the previous section, the catalytic reduction of nitric oxide with carbon materials was mentioned. However, in addition to the carbon monoxide, the reaction can also be conducted in the presence of oxygen. Such presence should be accounted for because in real world-scenarios (such as a vehicle or an industry's operation) oxygen is frequently present in the exhaust gases. However, its presence influences the reaction mechanism, and as a consequence, the operating temperatures.

In the presence of oxygen (Figure 2-9), the first step is the chemisorption of oxygen into the carbon surface, resulting in carbon monoxide, that will be subsequently adsorbed into the surface. Meanwhile, nitric oxide is also chemisorbed. The next step will be the reaction of the adsorbed nitrogen with the adsorbed carbon monoxide, originating adsorbed carbon monoxide and molecular nitrogen. This pathway is concluded with the desorption of the N_2 and the CO_2. From this reaction mechanism, it is possible to conclude that the presence of carbon monoxide has a significant role in nitric oxide reduction.

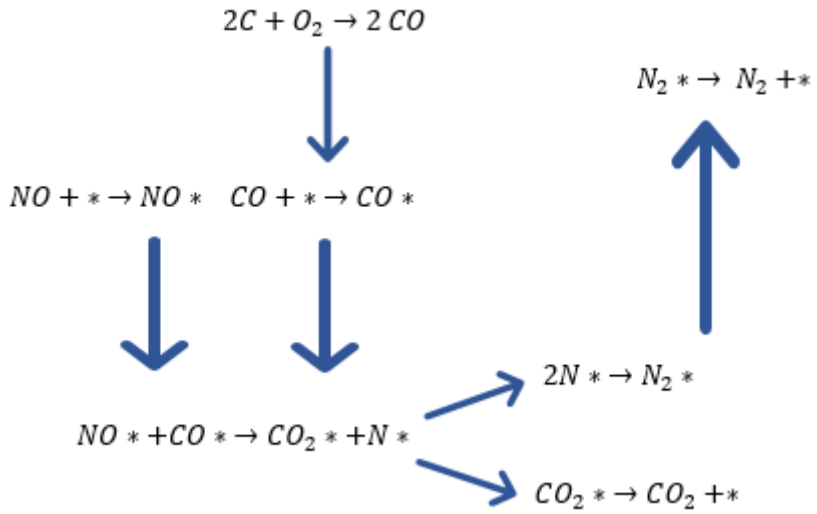

Figure 2-9 - *Mechanism for the catalytic NO reduction with carbon materials*

It was reported in the literature that the presence of oxygen could improve the nitric oxide reduction, conversions up to 90% were obtained when oxygen was present, and 5% when it was not [48] - with CNT conversions were up to 30% at 400 ^{0}C [42]. Some authors even managed to achieve complete conversion, although the temperature reached 650 ^{0}C [49]. As a result, as seen above, different inlet compositions not only affect the catalytic performance but also affect the pathway undertaken by the reaction.

2.2 Carbon materials

Carbon materials include activated carbon, char, graphene and carbon nanotubes, and xerogels. They have an array of appealing properties for catalytic applications. These properties include micro- and mesoporosity, large surface area (950-2000 m^2/g) as well as high adsorptive volume per unit volume, and they also have a tuneable porous structure [50]. Additionally, these materials can catalyse several reactions. Moreover, their chemical surface properties can be improved even further as carbon materials can be modified with heteroatoms [51]. This modification, in particular the doping with nitrogen, can result in an increase in the catalytic activity towards the catalytic reduction of nitric oxide.

2.2.1 Carbon xerogels

Carbon xerogels are solid-formed gels, synthesised by the polycondensation of resorcinol, which is followed by heat treatment, resulting in a crosslinked structure.

The carbon xerogels are very promising materials due to their excellent properties, such as mechanical resistance, porosity, and tunability [74]. It is possible to control the final textural properties of this material, varying the polymerisation conditions (pH, presence/absence of surfactant) as well as the heat treatment temperature [75].

2.2.1.1 Nitrogen-doped carbon xerogels

The presence of N-atoms in the surface of carbon materials increases the electron density, leading to higher electron mobility decreasing the electron work function at the carbon–fluid interface. Thus, N-doped carbons exhibit enhanced catalytic activity in electron transfer reactions, in the same way as semiconducting metal oxide catalysts. In literature, it has been reported that the presence of nitrogen groups enhances the activity of activated carbons towards the nitric oxide reduction reaction [52].

Furthermore, it is also possible for modifying the chemical properties of sol-gel solutions by adding different precursors. Such precursors such as nitrogen precursors are added during xerogel synthesis in order to obtain carbon materials with different nitrogen groups in their structure, such as lactam, graphitic nitrogen, pyridinic oxides, pyrrolic nitrogen, triazines, cyano- groups, amines, pyridinic nitrogen and metal coordinated nitrogen, as illustrated in Figure 2-10. Carbon materials with pyrrole and pyridine N-containing groups present the lowest band gap, thus the highest catalytic activity [45].

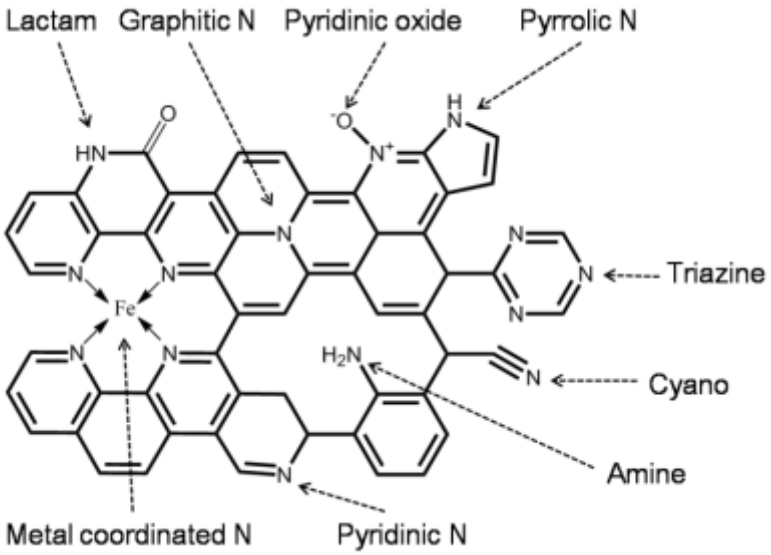

Figure 2-10 - *Different nitrogen groups on carbon materials' surface[53]*

2.3 Structured catalysts

Monoliths or other structured supports (Figure 2-11) can be an attractive alternative to conventional supports in heterogeneous catalysts. Monoliths have a large potential for catalytic processes due to large specific area, low-pressure drop, especially comparing to packed beds, excellent mechanical and thermal resistances. When compared to traditional systems, some authors have stated that structured catalysts yield superior catalytic performance[54].

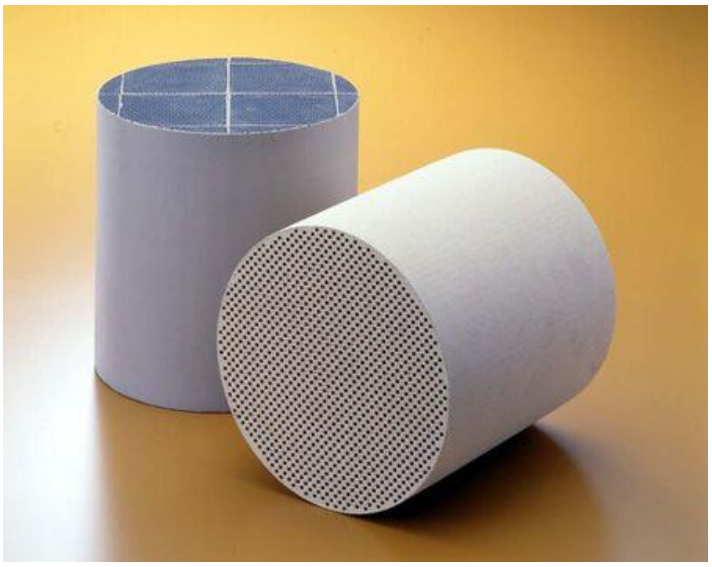

Figure 2-11 – *Silicon carbide and cordierite monolith structured catalysts [55]*

The structured support can be used as such, or the catalytic material can be deposited as a layer on the walls (usually by washcoating), or the catalyst can be grown on the walls. The washcoating method is based on the adhesion of the solid, previously dispersed in a slurry. In this work, we proposed an alternative method to obtain carbon-based structured catalysts. It is the intended growth of carbon in a melamine foam; that will be the template material.

3 Materials and Methods

In this section, the instruments and the followed methodology will be described. This will include the preparation of the sol-gel solution and the catalysts as well as the characterisation methods utilised. Afterwards, the procedures related to the catalytic tests will be also described.

3.1 Preparation of the structured catalysts

The sol-gel solution used to soak the melamine foam was prepared as follows: 45,45 g of resorcinol Sigma-Aldrich was added to 10 g of melamine 99% (Sigma-Aldrich) (10 g of urea 99.0-100.5%, Sigma-Aldrich) in 54,54 mL of distilled water. The solution was heated to 90 °C under stirring until the melamine (urea) was completely dissolved. Then, it was cooled to room temperature and 165 mL of formaldehyde were added. The pH was adjusted to 5.3 (6.0) with a 0.1 M of NaOH or HCl solution. To evaluate the use of a surfactant, samples were made with 10 g of Pluronic F-127 in its composition. This surfactant is non-ionic which will cause it to intervene in the polymerisation process, thus developing the chemical structure of the gel. In turn, that would lead to an increase in mesoporosity. On the flipside, its intervention in the polymerisation could lead to its competition with formaldehyde groups for the polymerisation reaction. Moreover, surfactants can also favour the dispersion of the reactants (and thus able to prevent aggregation).

The template material used to prepare the structured catalyst was a melamine foam supplied by BASF (6 cm x 2 cm x 2 cm). This material was soaked in the sol-gel solutions. The samples were impregnated using different soaking times (2 and 10 min); for some samples it was used compressed air to remove the excess of solution that could have stayed inside the pores. Afterwards, the samples underwent a gelation process (85 ºC during 3 d). The dried gel-foams were carbonized under nitrogen flow (100 cm^3/min) at 800 ºC.

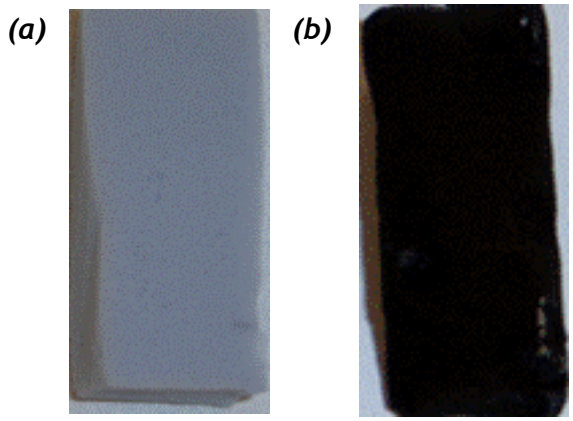

Figure 3-1 *~ Image of original foam samples (a) and after impregnation with sol-gel solution and carbonisation (b)*

It should be noted that the catalysts were prepared under different conditions. Such changes in the synthesis conditions were made to determine how they would impact the performance of the resulting catalyst. It has been described in the literature that pH influences the cross-linking of the resorcinol and formaldehyde in the sol-gel synthesis, thus changing the carbon structure. This can potentially culminate in an impact on the catalytic performance. Furthermore, different nitrogen precursors (melamine or urea) were tested due to the different percentages of nitrogen amount of the different compounds. Another factor to account for would be the nitrogen groups that each precursor is able to place on the carbon surface. Then, the soaking time was chosen in order to investigate the influence of different soaking times, since it can lead to an improvement in the catalytic activity, because longer soaking times lead to better sol-gel dispersions and loadings on the catalyst surface. However, excessive amounts could also be futile as the foam cannot retain any more solution. In Table 3-1 the synthesis conditions of the prepared catalysts are shown indicating the synthesis pH, the nitrogen precursor, the exposure to compressed air and the foam soaking time in the sol-gel solution.

Table 3-1 – Catalysts synthesis conditions

Sample	Nitrogen precursor	Surfactant inclusion in synthesis	pH	Soaking time	Exposure to pressurized air
XG6.0M2	Melamine	no	6.01	2	no
XG6.0aM2	Melamine	no			yes
XG6.0M10	Melamine	no		10	no
XG6.0aM10	Melamine	no			yes
XG5.3M2	Melamine	no	5.30	2	no
XG5.3aM2	Melamine	no			yes
XG5.3M10	Melamine	no		10	no
XG5.3aM10	Melamine	no			yes
XG5.3U2	Urea	no	5.31	2	no
XG5.3aU2	Urea	no			yes
XG5.3U10	Urea	no		10	no
XG5.3aU10	Urea	no			yes
XG6.0U2	Urea	no	6.01	2	no
XG6.0aU2	Urea	no			yes
XG6.0U10	Urea	no		10	no
XG6.0aU10	Urea	no			yes
XG5.3US2	Urea	yes	5.29	2	no
XG5.3aUS2	Urea	yes			yes
XG5.3US10	Urea	yes		10	no
XG5.3aUS10	Urea	yes			yes
XG6.0US2	Urea	yes	6.01	2	no
XG6.0aUS2	Urea	yes			yes
XG6.0US10	Urea	yes		10	no
XG6.0aUS10	Urea	yes			yes
XG5.3MS2	Melamine	yes	5.32	2	no
XG5.3aMS2	Melamine	yes			yes
XG5.3MS10	Melamine	yes		10	no
XG5.3aMS10	Melamine	yes			yes
XG6.0MS2	Melamine	yes	5.99	2	no
XG6.0aMS2	Melamine	yes			yes
XG6.0MS10	Melamine	yes		10	no
XG6.0aMS10	Melamine	yes			yes

3.1.1 Design of Experiments (DOE)

A Design of experiments (DOE) methodology was utilised to select the samples to be tested in catalytic experiments. Due to limitation of time caused by the pandemic situation, it was not possible to test all the prepared samples on the NO reduction. Moreover, this methodology also

gives important information concerning the impact of each synthesis variable in the catalytic performance. More specifically, a half-factorial design with a V resolution was undertaken. In this work, that means that even though 32 samples were prepared, only 16 were tested (the chosen samples are in Appendix H). This methodology was used so that the sample choice would still yield statistically significant interpretation of the effect of each selected variable.

3.2 Catalyst characterization

3.2.1 Thermal characterization

Thermal stability of the catalyst was determined by thermogravimetric analysis in a Netzsch model STA 409 PC. The samples were heated from room temperature until 900 ºC with a heating rate of 10 ºC min^{-1} under helium atmosphere. This temperature was kept during 7 min under helium atmosphere after this time the atmosphere was changed for air for 13 min. In order to evaluate the samples stability in oxidant atmosphere, the thermogravimetric analysis was also conducted under an air atmosphere instead of a helium atmosphere.

3.2.2 Textural characterisation

The textural characterisation of the samples was based on the nitrogen adsorption-desorption isotherms determined at -196 ºC with a Quantachrome Instruments Nova 4200e. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation (S_{BET}). The samples (~0.1 g) were outgassed at 150 °C for 3 h under vacuum.

3.2.3 Elemental analysis

Elemental analysis was carried out on a vario MICRO cube analyser from Elemental GmbH in CHNS mode. Each element (CHNS) was determined by combustion of the sample at 1050 °C and calculated by the mean of three independent measurements, using a per-day calibration with a standard compound. Oxygen analysis was carried out on a rapid OXY cube analyser from Elemental GmbH. Oxygen composition was determined by pyrolysis of the sample at 1450 °C and calculated by the mean of three independent measurements, using a per-day calibration with a standard compound.

3.2.4 Morphological characterization

The morphological properties of the materials were investigated by Scanning Electron Microscopy (SEM) using a Quanta 650 FEG (FEI).

3.3 Catalytic experiments

The catalytic activity performance tests were carried out resorting to the assembly shown in Figure A-1 (Appendix B), where the reaction occurs in a fixed bed reactor with an internal diameter of 0.6 cm inside an oven with temperature control by opening the valves of the desired gases and switching on the oven. The measurement equipment setup includes a nitrogen oxides analyser ("Chemiluminescence NO-NO_2-NO_x Analizer" Model 42i Thermo Scientific), carbon monoxide and carbon dioxide analyser ("Rapidox 3100"), and a mass spectrometer ("Dymaxion Dycor") equipped with a data acquisition software ("Dycor" analyser 2000). The latter collected the m/z signals of 12,14, 28, 30, 44 and 46, which correspond to carbon, nitrogen, molecular nitrogen, carbon dioxide and nitric dioxide, respectively. Signal 28 also corresponds to carbon monoxide. It should also be highlighted that the carbon monoxide in the inlet stream interferes with the NO and NO_2 readings of the analyser. This fact has influenced the catalytic test conditions defined and due that carbon monoxide was not used in all the experiments.

The reduction of NO over carbon materials was carried out in a fixed bed U-shaped flow type reactor. The sample weight, the flow rate, the O_2 concentration, the NO concentration in He were, respectively, 0.20 g, 100 cm^3/min, 5% v/v and 1000 ppm. The samples did not require pre-treatment, although before being placed in the reactor, the catalyst samples were ground to grain size in the 0.2-0.3 mm range.

3.3.1 Nitric oxide conversion

In this work, the catalyst's conversion of nitric oxide is one major aspect of its performance. Therefore, it is important to highlight how it was calculated. Below, Equation 3-1 shows how it is calculated. The necessary variables – nitric oxide concentration during the assay and at its start – are both obtained from the NO/NOx analyser.

$$x_{NO}(\%) = \left(1 - \frac{C_{NO}}{C_{NO_0}}\right) * 100 \qquad \textit{Equation 3-1}$$

4 Results and discussion

4.1 Catalyst characterization

4.1.1 Thermogravimetric analysis (TGA)

TGA was done as a part of the characterisation of the prepared catalysts. This test allowed to draw conclusions about the catalyst's thermal stability. For this end, the analysis was conducted under an atmosphere of air or helium (the latter was chosen due to being an inert gas). The thermograms of samples XG5.3aMS10, XG5.3aM10 and XG6.0aM2, - are represented in the Figure 4-2 and Figure ***4-1***.

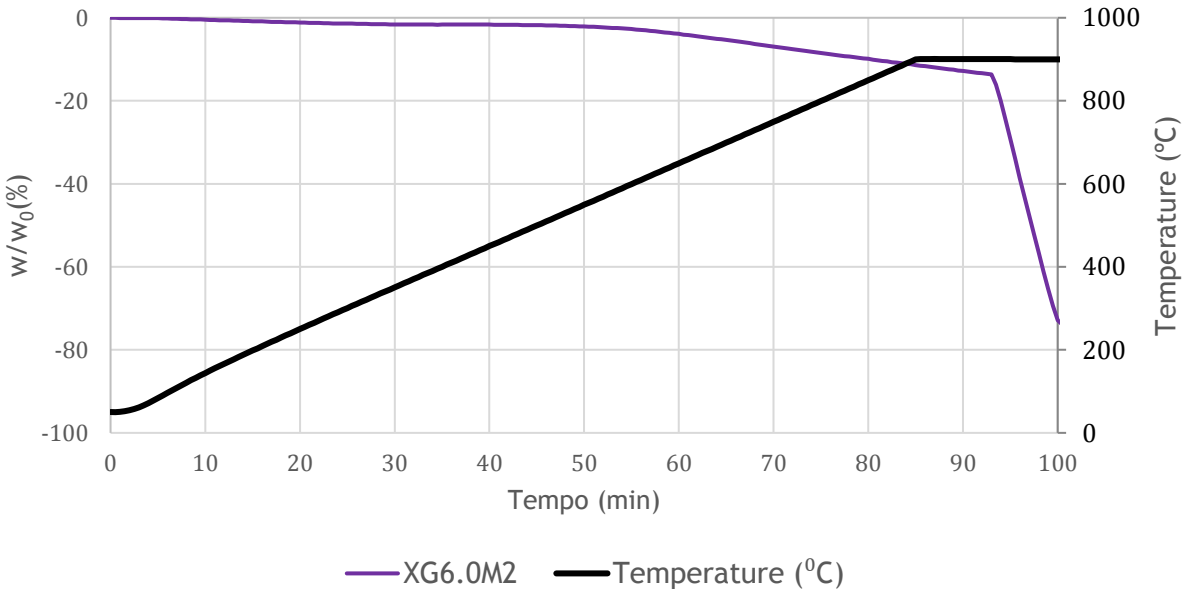

Figure 4-1 - *TG analysis in helium atmosphere*

Sample XG6.0aM2 was tested in an inert atmosphere as it is shown in Figure 4-1. From the resulting weight loss, it is possible to conclude that the sample is thermally stable. From the results in Appendix B, the remaining samples present similar curves and, consequently, the same degree of stability in helium.

In addition to the tests made in a helium atmosphere, the two samples - XG5.3aMS10 and XG5.3aM10 - were tested in air atmosphere. This test allowed to draw conclusions about the thermal stability in conditions that would be closer to the conditions these catalysts would experience during a reaction. The results are shown in Appendix B.

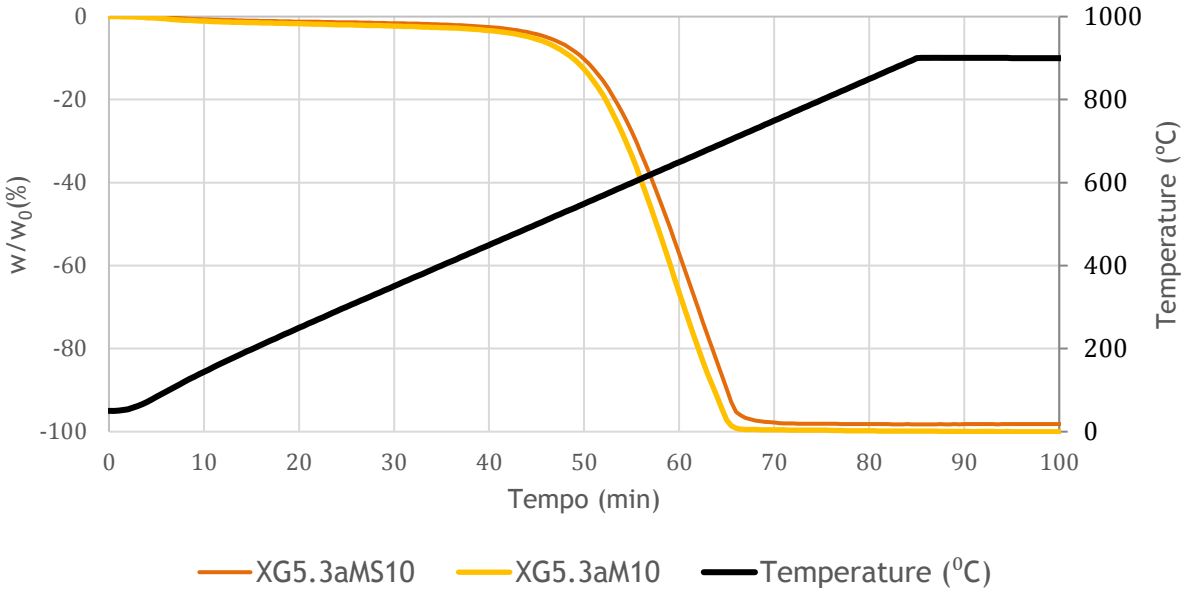

Figure 4-2 - *TG analysis under air atmosphere*

From the results, it can be observed that the thermal stability of the different samples is rather similar despite the surfactant's presence or absence. Overall, the weight loss only initiated after 570 ºC. Past that temperature, the samples would start to degrade, which obviates a loss in catalytic performance. Such loss has led to the decision to the conduction the catalytic tests up until 450 ºC.

4.1.2 Textural characterisation

The textural characterisation of the samples was obtained from N_2 adsorption isotherms at -196 ºC. As example Figure 4-3 shows an isotherm obtained for sample XG6.0M2.

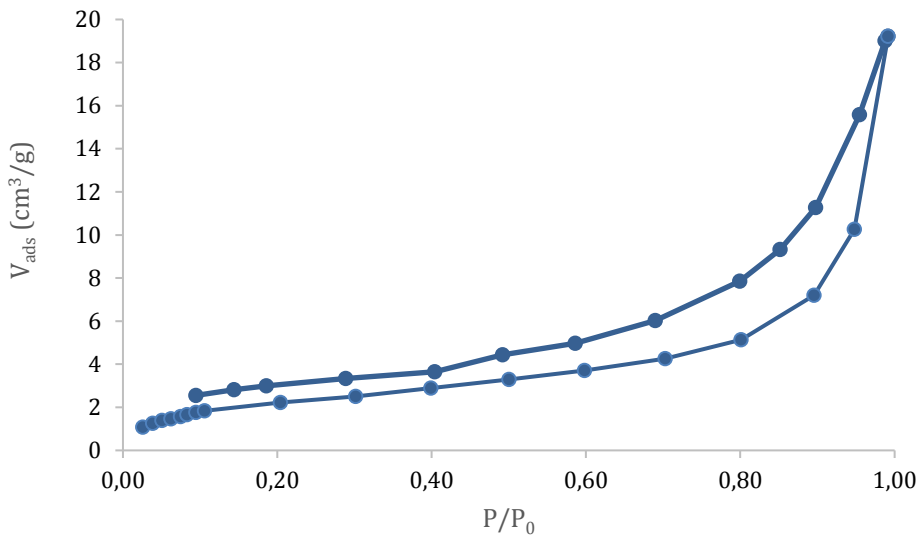

Figure 4-3 - *Nitrogen adsorption-desorption isotherms determined at -196 ºC of the XG6.0M2 sample*

Analysing Figure 4-3, it can be concluded that the isotherm is type II, characteristic of non-porous or macroporous materials. Observing the results represented in Table 4-1, it appears that the obtained materials are non-porous, since they present low surface values.

Table 4-1 - *Textural properties of prepared samples*

Sample	Total pore volume (cm^3/g)	BET surface area (m^2/g)
XG6.0U2	0.008	1
XG6.0aMS10	0.003	≈0
XG5.3MS2	≈0	9
XG5.3M10	0.007	4
XG6.0M2	0.024	8
XG5.3aMS10	0.001	≈0
XG5.3US2	0.022	29
XG6.0aMS2	≈0	≈0
XG6.0aM2	0.006	5
XG5.3MS10	0.004	≈0

Furthermore, it should be noted that the prepared materials show similar curves, despite the different synthesis conditions. This similarity could be explained by the templating method used in this work, since when structured catalysts are prepared via templating, the resulting material's pore structure is limited by the template's structure [56].

4.1.3 Elemental analysis

Elemental analysis was carried out in order to determine the composition of the tested samples. This information will provide further insight into the nitrogen-surface amounts. The obtained results are shown in **Table 4-2**. The samples were selected according to their synthesis conditions, because that way, their influence would become clear. A nitrogen-doped carbon xerogel (Appendix C) was tested in conjunction with the samples in order to understand the effect of the foam.

***Table 4-2** - Elemental analysis of prepared samples*

Sample	Carbon [%]	Hydrogen [%]	Nitrogen [%]	Sulphur [%]
XG5.3M10	78.0	1.7	4.3	0.03
XG5.3MS10	81.8	2.2	3.2	0
XG6.0aM10	84.2	1.4	4.0	0
XG5.3M2	75.2	1.6	3.7	0
XG5.3aM10	80.2	1.5	2.8	0
XG5.3U10	85.3	1.4	3.4	0
XG6.0U10	83.5	1.8	3.1	0
XG6.0MS10	80.8	1.7	3.5	0
XG6.0M2	74.3	3.1	4.9	0
XG6.0M10	79.6	2.5	5.3	0
Xerogel	83.1	1.0	3.5	0.02

The tested samples do not have any sulphur content. However, both the carbon xerogel and the XG5.3M10 do present a trace amount of it. That could be explained by contamination during their preparation or manipulation during the test. Furthermore, the soaking time had a global effect on the samples' carbon content: the samples with a 2-min soaking time present the lowest carbon percentages. This could be explained by the fact that the reduced soaking time has led to a lower sol-gel solution volume in the foam and therefore, lower amounts of carbon in the end result.

On the other hand, the samples synthesised with urea present lower amount of nitrogen than the ones prepared with melamine. Even though melamine has a higher percentage of carbon (in mass), urea yields higher carbon contents in the samples possibly due to having a higher affinity with the sol-gel solution; the difference in nitrogen could be explained by the higher amount of nitrogen in melamine molecules.

The influence of exposure to compressed air is difficult to isolate with the present data. However, it is possible to observe that, when combined with a pH of 5.3 it yields the highest C/N ratio. This could be explained by the fact that the compressed air's pore unobstruction

intensifies the C-C bond strengthening effect that the pH 5.3 has. Nonetheless, this effect does not seem as pronounced at pH 6, which further corroborates that inference. The surfactant's effect is equally difficult to isolate, but the samples prepared with it had the highest hydrogen percentages as well as among the highest C/N ratios.

As for pH, it seems to yield higher nitrogen contents when pH 6 is combined with melamine. This could be a consequence of the stronger C-N bonds that this value promotes, when compared to 5.3. Moreover, melamine has more C-N bonds than its counterpart, which means that the pH's beneficial effect would be more pronounced on the former.

Finally, the carbon xerogel's results should also be compared with the remaining samples. From the table above, it is possible to tell that ranks among the highest carbon percentages. Notwithstanding, it does not rank among the highest nitrogen contents. This could be explained by the fact that the melamine foam's composition has an impact on the sample. However, such effect is not always positive as some of the samples' nitrogen contents are lower than the xerogel's.

4.1.4 Morphological characterization (SEM)

The prepared samples were analysed by SEM to observe their structure. The SEM image of the melamine foam is shown in Figure 4-4.

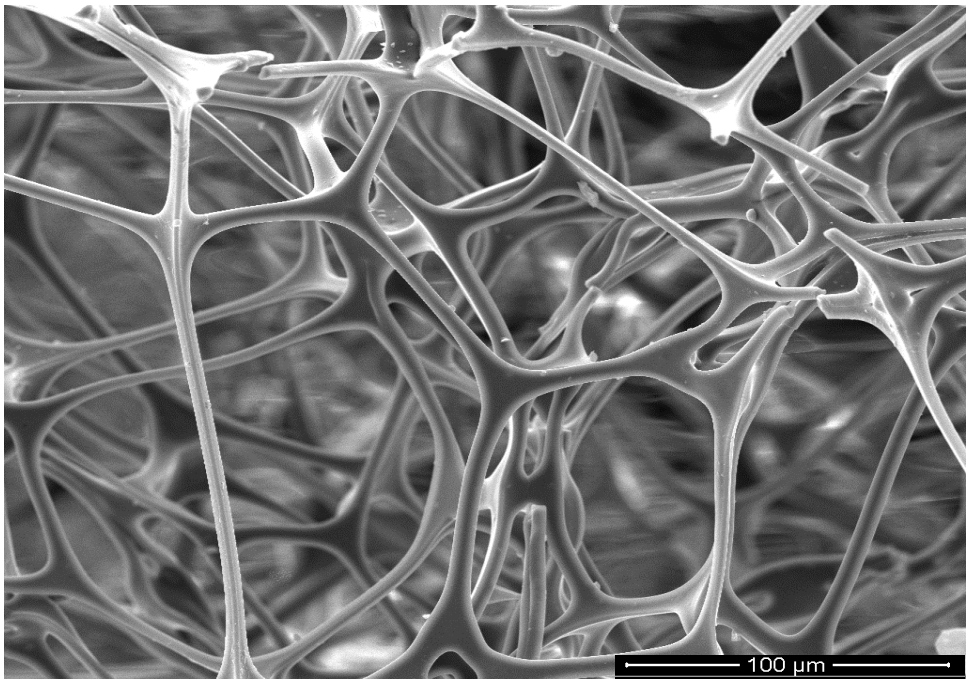

Figure 4-4 - *SEM image of the melamine foam*

The melamine foam sample presented in Figure 4-4 presents an interconnected structure with hollow space in between. The images obtained of N-doped carbon samples are shown in Figure 4-5.

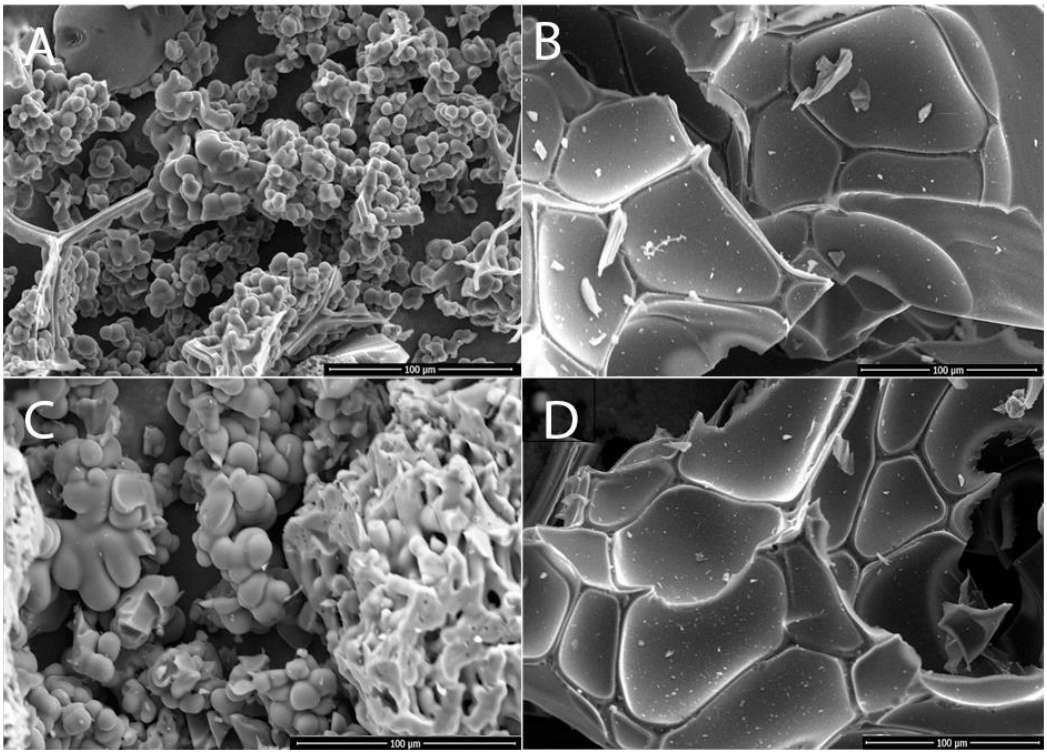

Figure 4-5 - *SEM images of. A: XG6.0aM2; B: XG6.0MS2; C: XG6.0M10; D: XG6.0aMS2 samples.*

SEM images of the N-doped carbon samples prepared revealed that the interconnected structure of the melamine foam is no longer present. Instead, the prepared xerogel comprises most of the images A and C. These images also present a few strands of the melamine foam network. Despite this fact, they still present defined xerogel particles. As for images B and D, the structure appears to have separated into independent pieces instead of singular units. Furthermore, they show no signs of the melamine foam, almost as the xerogel had completely covered the hollow spaces.

Upon comparing all four images, it becomes clear that images A and C are rather different from images B and D. More specifically, the xerogel particles in A and C are well defined and smaller than the ones visible in the other two images. This difference could be explained by the fact that the samples in B and D were prepared with a surfactant whereas the other two were not. This shows that the non-ionic surfactant had a detrimental effect in the resorcinol-formaldehyde polycondensation (possibly because it competed with the formaldehyde). This

means that, in order to make the use of non-ionic surfactants viable, its concentration will have to be lower.

Upon comparison with literature [57], it was expected that the xerogel particles would latch onto the strands of the melamine foam network. However, that was not observed in any of the images shown. That signals that the structure of the foam collapsed.

4.2 Catalytic tests

4.2.1 Influence of reaction parameters

The catalytic tests were carried out in order to determine the performance of the prepared catalysts in nitric oxide reduction. They were carried out at a constant flow rate of 100 cm^3/min and the temperature would rise at 5 ºC/min until the final temperature was reached. The first tests were carried out to validate the experimental conditions. The results can be observed in Figure 4-6.

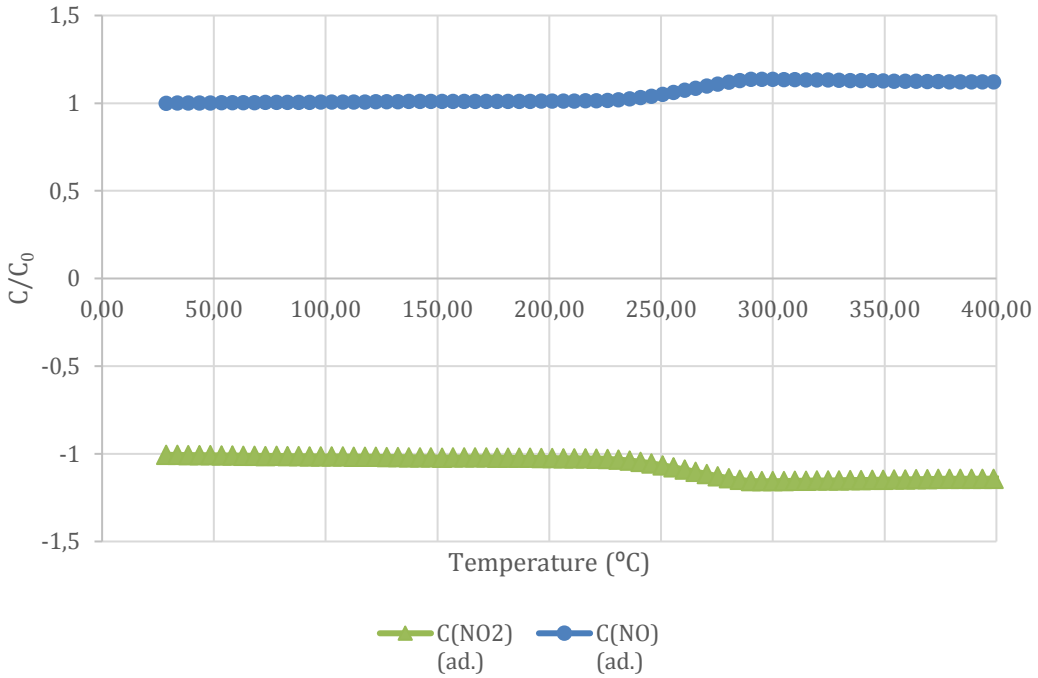

Figure 4-6 - *Adimensional NO and NO_2 concentrations during reduction during blank test using CO = 1000 ppm and NO = 1000 ppm*

This blank test was carried out at a flowrate of 100 cm^3/min; both the inlet concentration of carbon monoxide and the inlet concentration of nitric oxide was 1000 ppm; the temperature

rose at 5 ºC/min until 400 ºC was reached. The results show negative values on the analyser NO_2 readings, which seemed to be caused by a source of interference in the nitric dioxide measurement. At the face of these results, further assays were made to investigate the interference source. As such blank assays with 1000 ppm of nitric oxide and varying amounts of carbon monoxide were made. The results are shown in Figure 4-7 show that the NO_2 response varies with the concentration of carbon monoxide.

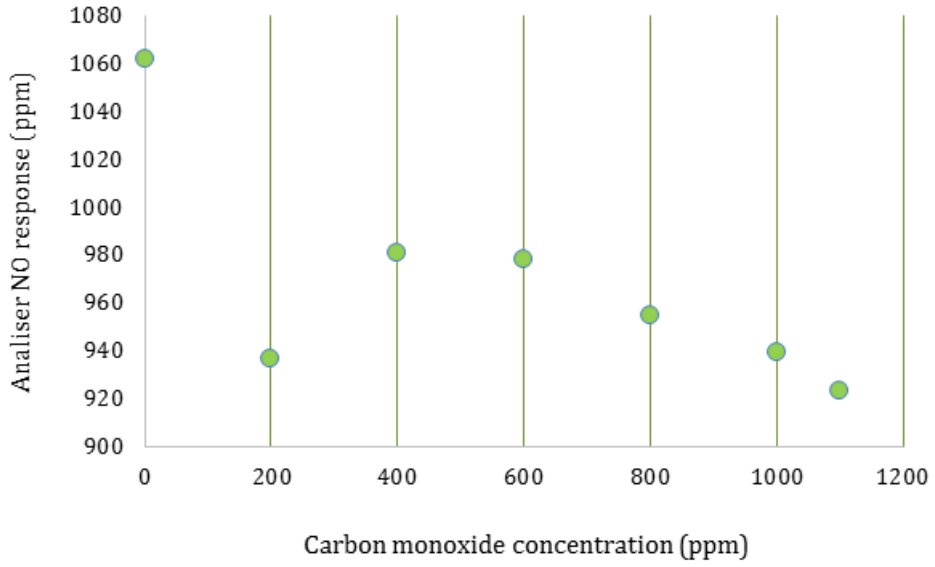

Figure 4-7 - *Blank assays in the presence of varying carbon monoxide concentrations. NO= 1000 ppm*

If carbon monoxide did not interfere in the measurement, the graph would have been a straight line. However, the obtained graph shows otherwise. More specifically, when there is no carbon monoxide in the inlet stream, the analyser responds solely to the nitric oxide. However, when carbon monoxide is present, a trend in the variation of the analyser signal with the variation of the carbon monoxide's concentration becomes apparent. Now, the results in Figure 4-6 must also be considered. Like mentioned above, those results show that there is something clearly influencing the NO_x results. That said, when combining the information from both tests, it becomes more apparent that there is an unambiguous interference of the carbon monoxide in the instrument signal.

From there, an assay was carried out without carbon monoxide, nitric oxide at 1000 ppm, oxygen at 2% (v/v) and a flowrate of 100 cm^3/min with the sample XG6.0M2 to ascertain whether the samples would exhibit catalytic activity without it. As seen in Figure 4-8, the sample show activity under such conditions. Consequently, the catalytic assays were done without carbon monoxide to ascertain, which would be the best performing samples, to ensure the accuracy of the measurement.

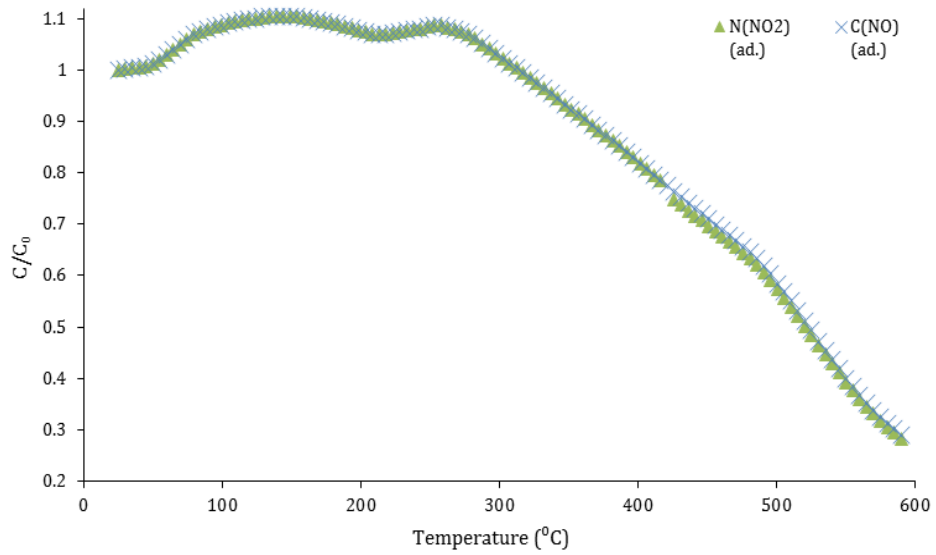

Figure 4-8 - *Adimensional NO concentration during reduction using 2% of oxygen and NO= 1000 ppm over XG6.0M2;*

It was observed that in the 150-200 ºC temperature range the nitric oxide concentration overpass the inlet NO concentration. Consequently, it was hypothesised that the N-doped carbon sample was adsorbing nitric oxide at low temperatures and realising the gas with the increase of the temperature. That hypothesis was tested by exposing the catalyst sample to 1000 ppm of NO for 1 h, followed by the shutting off the NO inlet and heating under He at the 5 ºC/min rise. In Figure 4-9 reveals an increase in NO concentration despite the absence of nitric oxide during the heating, thus proving that effectively there is adsorption occurring at low temperatures.

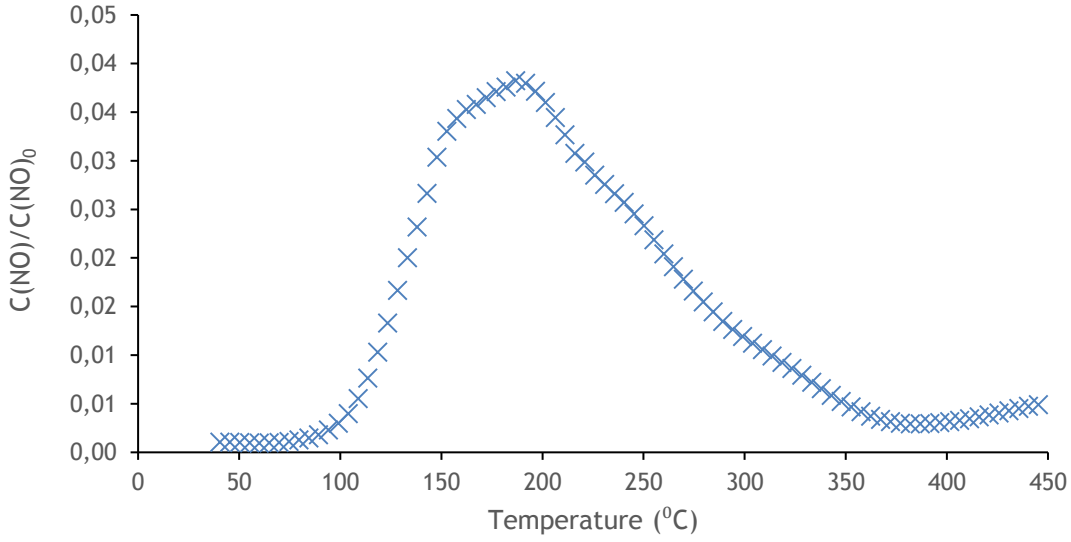

Figure 4-9 - *Evaluation of NO adsorption/desorption over XG5.3aM2. NO= 1000 ppm*

4.2.2 Assessment of catalysts performance

After these experiments, the sources of interference had been identified, the maximum assay temperature had also been defined and the spike in the NO concentration had been explained. Accordingly, after that, all the tests were carried with oxygen at 5% (v/v), NO at 1000 ppm with rising temperature (from room temperature to 450 ^{o}C at 5 ^{o}C/min) in order to determine how the different synthesis variables (pH, soaking time, surfactant presence, nitrogen source and compressed air exposure) would impact the catalytic performance of the prepared samples. The selection of the samples to test was made according to the DOE methodology described previously. The results from the sample XG6.0M10 is depicted in Figure 4-10. Initially, it was intended to choose the best performing sample. However, to ensure that there was enough sample mass for all the required assays this sample was chosen instead.

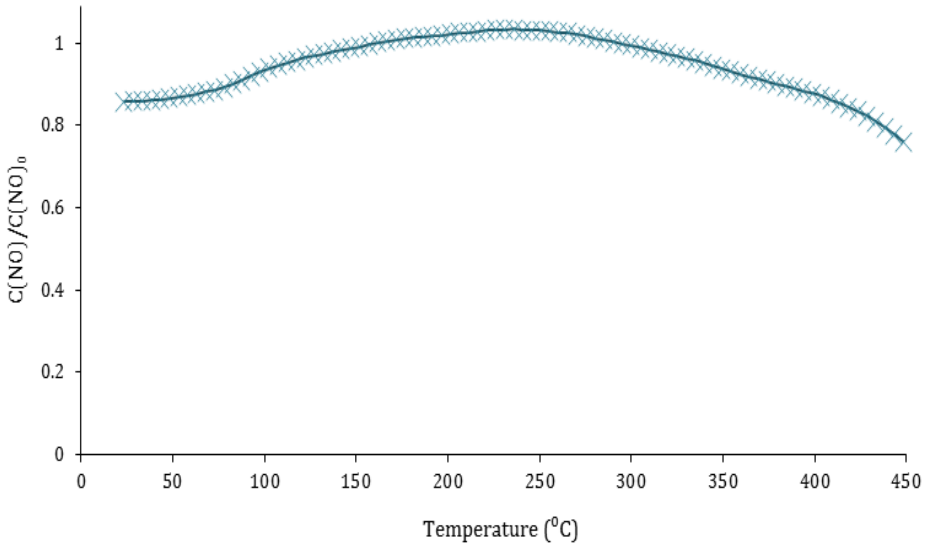

Figure 4-10 *- NO reduction over sample XG6.0M10. Flowrate= 100 cm^3/min; NO= 1000 ppm; O_2: 5% (v/v)*

It should be noted that right at the beginning of the assay, the dimensionless nitric oxide concentration starts at 0.85. This happens due to the room temperature conversion/adsorption that the catalyst exhibit when the gas stream is opened.

When analysing the results, it can be seen the NO adsorption in the expected temperature range. Also, it can be seen that the final NO concentration is lower than the initial one, meaning that temperature had a positive effect on conversion. Even then, the obtained conversion (24.0%) is still somewhat below the best performing one (29.0%). It should be further added

that these results are on par with the results obtained from (non-doped) CNT, which have been able to achieve 30% conversions at 450 ºC [42].

From the MS signals (Appendix D), it can be observed that the signals 28 (molecular nitrogen), 44 (carbon dioxide) and 46 (nitric dioxide) increase exponentially with temperature. However, since the present data only allows for qualitative analysis, it becomes problematic to tell whether the selectivity is shifting towards nitrogen or nitric dioxide. Regarding the formation of CO_2, it could be explained by some of the pathways in the previous sections mention the formation of carbon monoxide despite the absence of CO.

The NO conversions obtained for the remaining tested samples are shown in Table 4-3.

Table 4-3 - *Nitric oxide conversion obtained during the catalytic assays in the presence of the prepared catalysts. Flowrate = 100 cm^3/min; NO = 1000 ppm; O_2 = 5% (v/v); temperature= 450 ºC*

Sample	X NO (%)
XG6.0aMS2	19.9
XG5.3US10	24.4
XG6.0U2	17.3
XG5.3aM2	10.5
XG6.0M10	24.0
XG5.3MS2	20.4
XG6.0aUS2	22.0
XG6.0US10	29.0
XG5.3aM10	18.9
XG6.0MS2	26.9
XG5.3aUS2	15.1
XG5.3US2	22.7
XG5.3MS10	16.2
XG5.3U10	25.2
XG5.3aU2	17.7
XG5.3aMS10	0.0
XG6.0aM2	17.4
XG5.3aUS10	27.8
XG6.0aU10	25.5
XG5.3M2	18.4

Globally, the conversions obtained are comparable to the results obtained by other authors using doped and non-doped materials [42, 58]. From what can be inferred regarding the synthesis conditions, the influence of pH deviates from expectations. It would be expected that the samples prepared with a pH 5.3 would consistently yield a higher conversion as lower pH values strengthen the C-C bonds (however weakening C-H or C-O bonds). Instead, the higher

conversions were observed when pH 6 was combined with urea. That would be explained by the intensification of the C-H and C-O bonds caused by the higher pH and the lower carbon content they have shown in the elemental analysis. These two factors combined would mean that favouring the aforementioned bonds instead of the C-C bonds would be more beneficial.

As for soaking time, the behaviour corresponded to the expectations. It was predicted that a longer soaking time would lead to a higher volume of the sol-gel solution to be loaded onto the foam, thus leading to higher amounts of carbon groups. The elemental analysis results also confirm this prediction. Accordingly, they experienced a consistently higher conversion than the 2 min counterpart.

Regarding the presence of the surfactant, it revealed not to have the desired effect. From the SEM imaging, it had a negative effect on the xerogel structure, contrarily to the assumption that their positive effect on the structure development would be more significant than the possible competition they would have with formaldehyde. Nonetheless, from the presented results, it becomes rather challenging to determine whether its presence is beneficial or not.

As for the exposure to compressed air, the results show that it seems detrimental to conversion. Its use aimed to unobstruct the foam pores. However, it seems that the higher pore coverage will benefit the catalytic activity. Moreover, from the elemental activity results, the presence of compressed air also seems to increase the C/N ratio (this effect is stronger at pH 5.3 than at pH 6.0). This means that its effect may also stem also influence on the catalyst structure.

Moving on to the nitrogen source on conversion, it seems to influence both the conversion and the structure, as predicted. From the elemental analysis, it was concluded that the samples synthesised with urea had a higher carbon content as well as a lower nitrogen content. The lower nitrogen content, when compared with the samples prepared with melamine, may be explained by the urea molecule's lower nitrogen content. However, as highlighted earlier, pH 6 with urea has yielded the highest conversions of all tested samples.

Nonetheless, the higher conversion with lower nitrogen was unexpected. Since nitrogen lowers the reaction's band gap, it would make sense that a higher content would improve conversion. This would mean that the effect on the band gap is only observable within a nitrogen content range. Furthermore, it could also imply that the interaction with the surface carbon should not be neglected and thus, an increase in the carbon content at the nitrogen's expense would not be detrimental to the catalytic activity.

For one of the most promising samples, several experiments were carried out to evaluate the influence of the operating conditions in the catalyst performance.

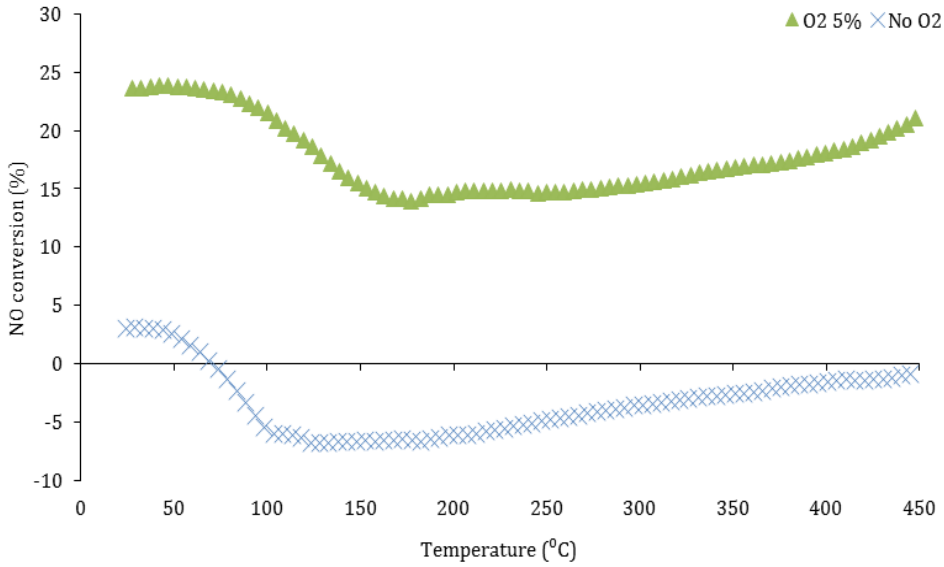

Figure 4-11 - *Comparison of the presence and absence of oxygen in the assay using the sample XG5.3aM10 with a flowrate = 100 cm^3/min, NO = 1000 ppm, CO = 1000 ppm; O_2 (when present) of 5% (v/v)*

It can be observed in Figure 4-11 that evolution of NO concentration in the experiment without oxygen is similar to the obtained in the presence of 5% of O_2. However, the presence of oxygen clearly benefits the reaction.

Observing the N_2 and CO_2 and signals in the MS results (Appendix E) it could be assumed that the nitric oxide and the carbon monoxide are being converted to these species, respectively. Nevertheless, the increase in the NO_2 signal also means that there is a conversion towards nitric dioxide. Furthermore, the signal heights are always higher in the assay carried out with oxygen, which further confirms the positive influence of oxygen. Regarding the carbon monoxide's influence, it can be said that it is beneficial. More specifically, when CO was present the conversion at 450 ^{0}C was 25% versus 18.9% without it. This difference is considerable could be attributed to the different reaction pathways followed when carbon monoxide is present.

A conversion of approximately 20% for carbon materials when NO, CO and O_2 are present during the catalytic reduction of nitric oxide has been reported [48] , indicating that the obtained results only slightly outperform the previously reported results.

Then, the behaviour of XG5.3aM10 when exposed to 20% O_2 at ambient temperature was also investigated. The results are presented in Figure 4-12.

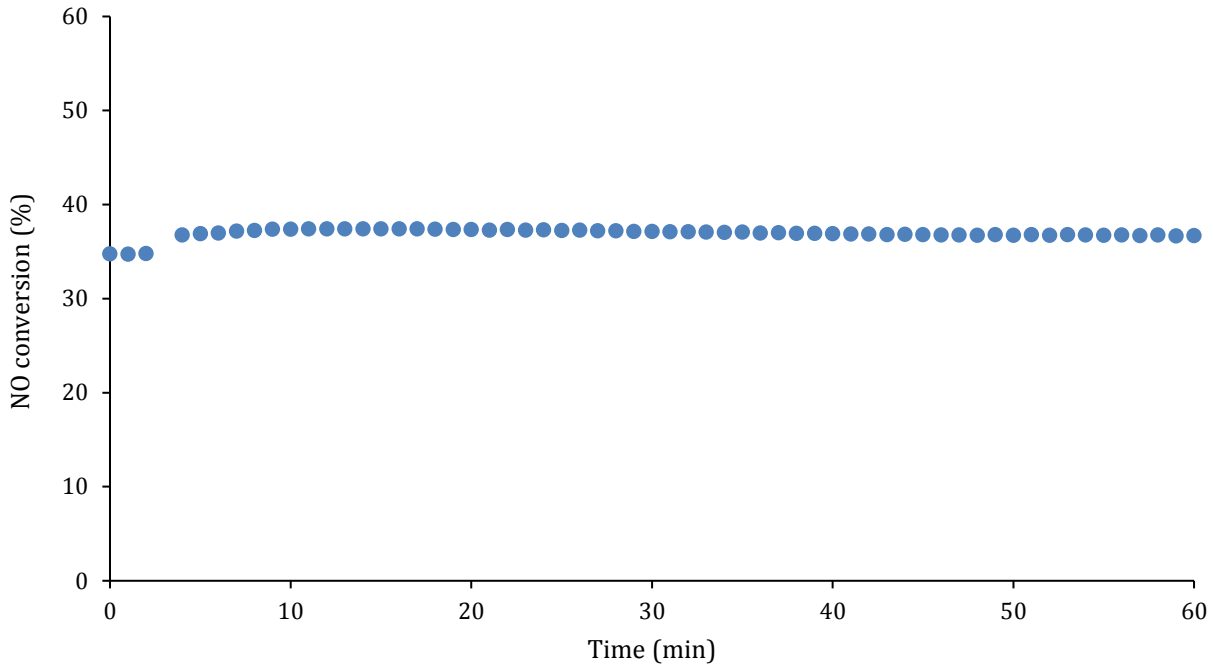

Figure 4-12 *- Isothermic test at ambient temperature (29 ºC over XG5.3aM10 at a flowrate = 100 cm^3/min, NO concentration = 1000 ppm, O_2 concentration = 20% (v/v)*

As it can be seen in the graph, despite the ambient temperature, there is still a level of nitric oxide conversion even though the previous catalytic tests do not show activity at room temperature. That means the conversion of NO seems to occur in a homogeneous fashion and not due to the presence of the catalyst when high oxygen content is present. The nitric dioxide reading from the analyser indicates that most of this conversion is occurring towards nitric dioxide. As it can be qualitatively analysed from the MS results (Appendix F), the formation of nitrogen is not very significant. The nitric oxide is being converted. Consequently, these results indicate that, at an oxygen concentration of 20%, room temperature seems to favour the formation of NO_2.

For comparative purposes, a catalytic experiment was carried out using a traditional carbon xerogel (it was prepared under the conditions mentioned in Appendix D). This material was chosen for this assay to determine whether the foam templating has an impact on the nitric oxide conversion. The surface area of this material is 246 m^2/g.

Figure 4-13 shows the obtained results.

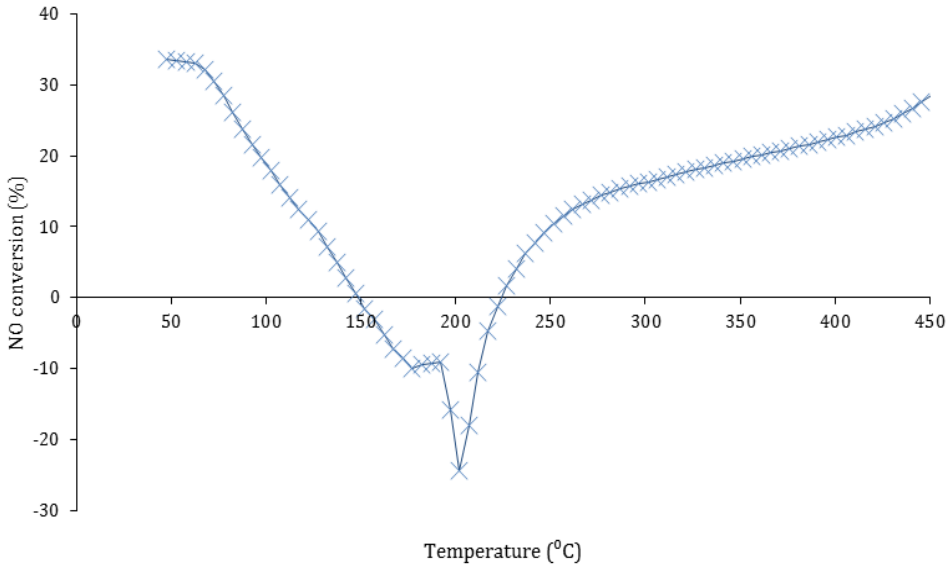

Figure 4-13 - *Results of the catalytic assays done with a xerogel with a flowrate = 100 cm^3/min, NO concentration = 1000 ppm, CO concentration = 1000 ppm, O_2 concentration = 5% (v/v)*

Similarly to the other tested samples, the xerogel also exhibits adsorption. However, the adsorbed amount seems higher (thus justifying the unexpected negative conversion), which could be explained by the higher surface area the carbon xerogel as compared with structured catalyst. Moreover, the conversion at 450 ºC (28.51%) is marginally higher to that of the tested samples. This observation is still consistent when compared with the sample XG6.0M10. As such, the foam does not greatly interfere with the conversion. Additionally, the lower surface area from the samples also does not seem to represent a hindrance to the conversion, even though it does not present the desired structure. That said, given how the foam provides better mechanical properties, it is still a valuable addition to the catalyst.

Upon analysing the MS results (Appendix G), the effects of the adsorption are still visible. Additionally, the amount of carbon dioxide and nitric dioxide formed seemed to increase with temperature, even though the nitric oxide signal would remain constant. Not much can be concluded from the signal 28 as it simultaneously contains the response from the CO and from the N_2. From this data, it can be said that, as the temperature rises, the NO conversion is the same, but the selectivity towards nitric dioxide increases with temperature.

4.2.3 Design of experiments (DOE)

From the application of this methodology, it was concluded that, among the tested samples, the factors that have a higher impact on the performance of the catalyst during the NO

reduction are pH of 6.0, use of urea instead of melamine, no exposure to compressed air and soaking time of 10 min. Furthermore, it should be noted that none of these parameters has shown an effect above statistical significance limit. This could be explained either by the small number of tested samples and/or by the low conversion values achieved during the catalytic tests, which would not allow for enough resolution to differentiate different samples with the confidence interval being used (95%). Nonetheless, the main effects are still consistent with the obtained results.

To dissect these results further, a pH value of 5.3 was expected to yield better conversion than the 6.0 counterparts as the lower pH strengthens the C-C bonds during the resorcinol and formaldehyde crosslinking process. However, this comes with the drawback that the C~H or C-O bonds will be weaker. Now referring to their structure, urea molecules contain an oxygen atom whereas melamine molecules do not. That means that, when exposed to a pH of 6, urea would develop a stronger C-O bond with the carbon material. This explanation would also justify the positive effect urea has had on conversion even though it has a lower nitrogen content than melamine.

The compressed air's effect could be explained by their effect on the sol-gel pore coverage. More specifically, exposure to compressed air causes the sol-gel to unobstruct the catalyst's pores. This change in dispersion was expected to influence the dispersion of the gel throughout the foam. However, the obtained results show that this unobstruction is detrimental to the catalyst performance. Thus, it could be concluded that, up to a certain extent, promoting higher amounts of sol-gel in the pores will improve conversion.

As for the soaking time, the result corresponded to the expectation, i.e., a longer soaking time would allow for the foam to retain a higher volume of the sol-gel solution. That higher volume is analogous having higher catalyst loadings in supported metallic catalysts, which lead to higher conversions if not increased too much. That could also be extended to the prepared catalysts, where excessively high soaking times would become a hindrance to the catalyst's performance.

The surfactant's effect was unexpected. The surfactant utilised in this work was non-ionic. That would lead to a better dispersion as well as an improvement in the development of the crosslinked structure. However, as mentioned before, the surfactant could also compete with the formaldehyde. From the obtained results, it was concluded that the presence or absence of the surfactant (in the tested concentrations) did not have a significant impact on the outcome regarding the conversion, albeit originating a considerable difference in the resulting structure.

5 Conclusion

In this work, structured catalysts were prepared from melamine foam to obtain N-doped structured carbon materials. This foam was chosen not only due to its structure, flexibility, low weight, high surface area and adsorbent properties, all of which make it a promising choice as a template or catalytic support. The prepared catalysts have then undergone analytic tests such as TG, SEM, adsorption isotherms and elemental analysis. This was carried out in order to develop better methods to synthesise structured catalysts, develop a methodology to successfully introduce nitrogen groups on the catalyst surface and offer insight into the reaction pathways for the catalytic reduction of nitric oxide. Most importantly, this work was also carried out to study the reduction of nitric oxide using the synthesised catalysts.

As for the TG tests, it is visible that the synthesis method has markedly impacted the resulting material composition. Moreover, these catalysts should operate under 450 ^{o}C in order to preserve their structural integrity.

The prepared catalysts had a rather small specific area (≈0-50 cm^2/g), which shows that the synthesis procedures must be improved.

The synthesis variables can indeed influence the composition of the samples. Moreover, it could also be concluded that melamine as nitrogen precursor and a pH value of 6 would yield the highest nitrogen content. Additionally, it was also concluded that both the carbon and the nitrogen content had a significant effect on the performance of the catalysts.

From the SEM imaging, it was observed that the structure collapsed; furthermore, it can also be concluded that the small surface area was caused by the structural collapse. As such, the samples resulted in a disordered xerogel structure instead of xerogel latched on the structured foam network. This statement is further confirmed by the fact that the prepared samples displayed a catalytic performance close to the tested xerogel. Nevertheless, such collapse did not turn out to become a hindrance to the xerogel's performance per se, which the synthesis method requires further fine-tuning to prevent the structural collapse of the samples. Furthermore, the prepared samples can adsorb NO at room temperature, which means they do not have the same light-off temperature issues other pre-existing methods possess.

In the catalytic tests, a nitric oxide conversion in the 15-29% range was obtained using the prepared catalysts. This is comparable to the performance of other carbon materials reported in the literature, revealing that these N-doped structured catalysts are promising for NO reduction, despite their low surface area. However, it could still be observed that a larger surface area could lead to higher amounts of NO adsorbed at room temperature. Furthermore, these materials exhibit adsorption of nitric oxide at room temperature, that will be desorbed

in the 150-200 ^{o}C range. This means these catalysts that were made from cheaper materials can realistically compete with costlier carbon materials such as carbon nanotubes. It was also concluded that the nitric oxide was being converted into molecular nitrogen and nitric dioxide, where higher temperatures favour the conversion towards nitric dioxide rather than molecular nitrogen. Moreover, when carbon monoxide was present, it would also be converted into carbon dioxide. Similarly to NO_2, the conversion to CO_2 would increase with temperature.

6 Assessment of the work done

6.1 Objectives Achieved

This work's objectives included the development of preparation methods for structured catalysts, the creation of a methodology to introduce nitrogen groups on to the catalysts surface and understanding the possible pathways for the nitric oxide reduction and carbon monoxide oxidation when the prepared materials are used.

32 samples were prepared under different synthesis conditions. From there, the catalytic tests were made. From those tests, it was possible to ascertain the influence of the different variables into the catalyst performance. Afterwards, the operation conditions were optimised in order to improve the catalytic performance. However, the structural collapse of the samples exhibit shows that further work needs to be done in the development of the structured catalysts synthesis and the nitrogen doping methodologies. The pathway understanding was somewhat stunted due to equipment limitations and due to time limitations related to the pandemic situation, which have limited access to the laboratories during a long period.

6.2 Final Assessment

The developed work was a rather important learning experience as I was able to learn about various techniques. This work also allowed me to work in different environments which has also taught me many things. Moreover, the work developed can also be used as a foundation for further development of catalysts for nitric oxide reduction.

In the future, the work developed could be improved further by adjusting the pH with different bases (preferably bases that do not contain sodium) and acids. Moreover, it has been reported that the polarity of the surfactant also influences the textural properties, so anionic and cationic surfactants should be experimented with. Moreover, multiple surfactants should also be attempted in order to further fine-tune the textural characteristics of the obtained material. Long-term experiments should also be carried out to evaluate catalysts stability during NO reduction.

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Appendix A Experimental setup

Figure A-1 shows the experimental setup for the catalytic tests

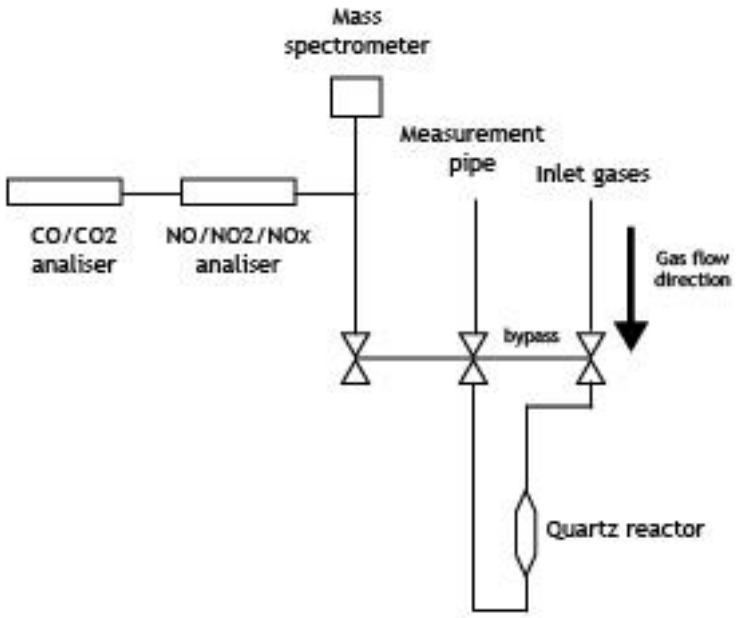

Figure A-1 - *Experimental setup for the catalytic activity assays*

Appendix B TG tests

TG assays were done to various samples in order to determine their composition as well as their thermal stability. The results are shown below.

Table B-1 - obtained compositions of the samples tested by TG

Sample	Water (%)	Volatile compounds (%)	Carbon (%)	Ashes (%)
XG6.0M2	0.21	13.15	60.8	25.6
XG6.0aM2	0.52	25.20	45.3	29.8
XG5.3M2	0.64	31.19	56.1	13.1
XG6.0U2	0.45	22.62	75.1	1.7
XG6.0MS2	0.29	27.67	67.7	4.6
XG6.0M10	0.51	22.06	74.0	3.4
XG5.3aM2	0.24	7.85	85.0	7.4
XG5.3U2	0.13	18.01	77.3	4.6
XG6.0MS10	0.38	29.56	67.4	2.7

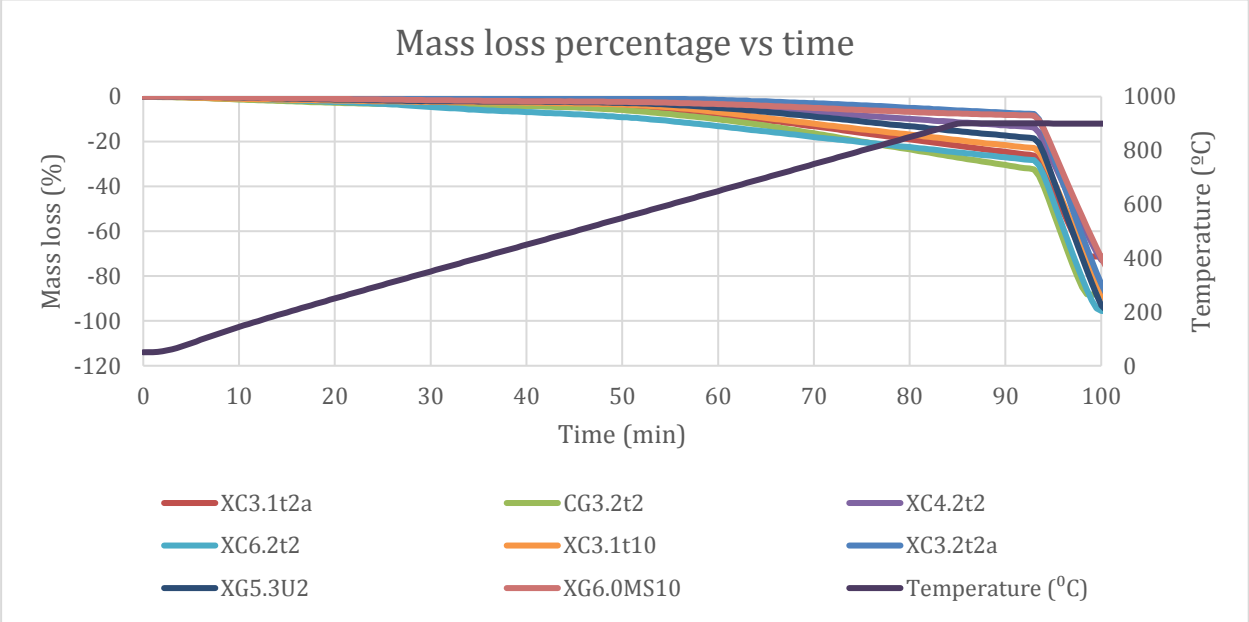

Figure B-2 - TG results obtained from all tested samples

Appendix C: Carbon xerogel preparation

It was necessary to determine the influence of the foam in the performance of the prepared catalysts. As such, a xerogel was tested. That xerogel was prepared by adding 18 ml of distilled water to 15g of resorcinol (under stirring). Once the mixture was homogenised, 3 g of melamine were added. Immediately after, the solution was heated to 90 ºC until the melamine was completely dissolved. Next, the solution was cooled to room temperature. Once reached room temperature, 20 ml of formaldehyde 37% were added under stirring, followed by pH adjustment. The pH was corrected to 6 with sodium hydroxide (2 mol/L) and hydrochloric acid (0.1 mol/L). The gelation was done in a water bath at 85 ºC for three days. The drying process was done in an oven for 4 days (1st day at 60 °C, 2nd day at 80 °C, 3rd day at 100 °C and 4th day at 120 °C). From there, the dried gel was carbonised under a nitrogen flow (1000 cm^3/min) at 900 ºC in a tubular furnace. The carbonisation was done at a heating rate of 2 ºC/min until 200 ºC, where this temperature was kept for 2 hours. Then, at the same heating rate, the temperature was risen to 300 ºC. Once reached, this temperature was held for 1 hour. Then, still at the same rate, the temperature was elevated to 900 ºC. This last temperature was held for 2 hours.

Appendix D: XG6.0M10 assays

The results of one of XG6.0M10, one of the best performing samples are shown in order to better understanding the underlying rationale for the catalyst's performance. Below, the MS results are shown.

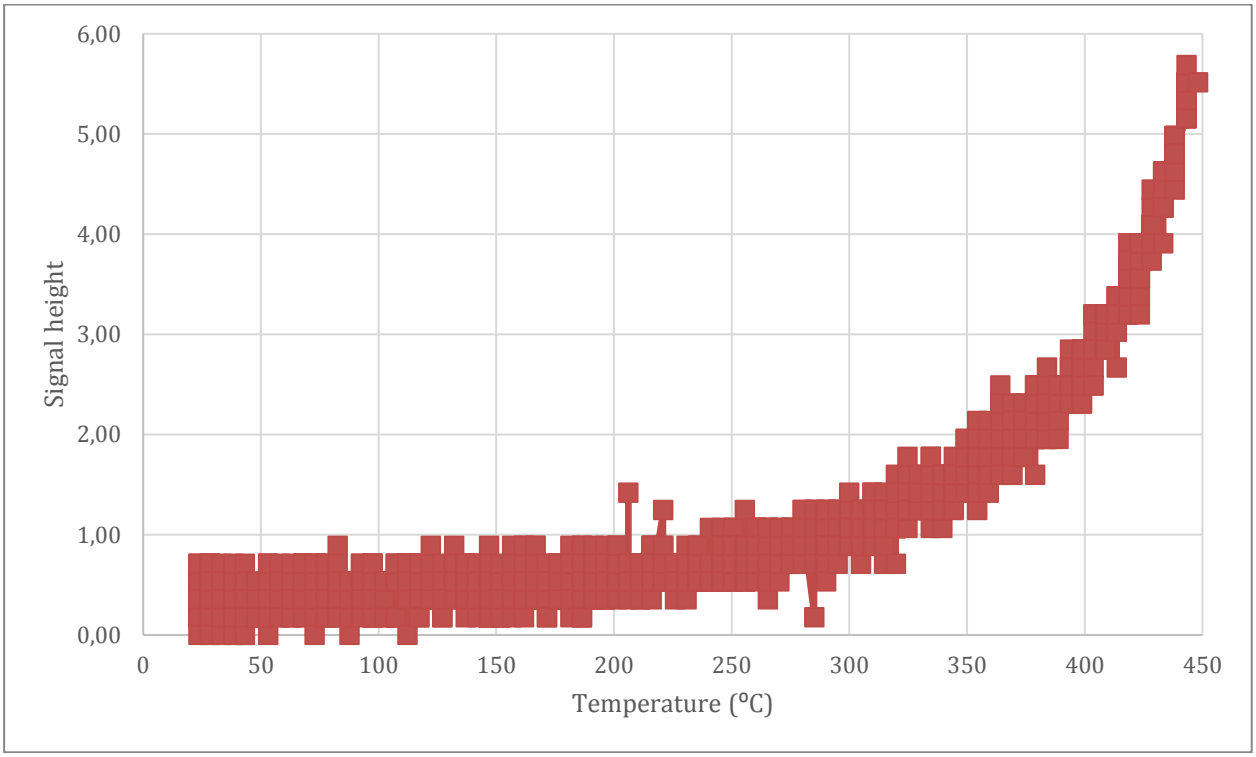

Figure D-1 - Dimensionless signal height on mass 28 (molecular nitrogen and carbon monoxide) over the sample XG6.0M10 with a flowrate100 cm^3/min, NO concentration = 1000 ppm, CO concentration = 1000 ppm and O_2 concentration of 5% (v/v)

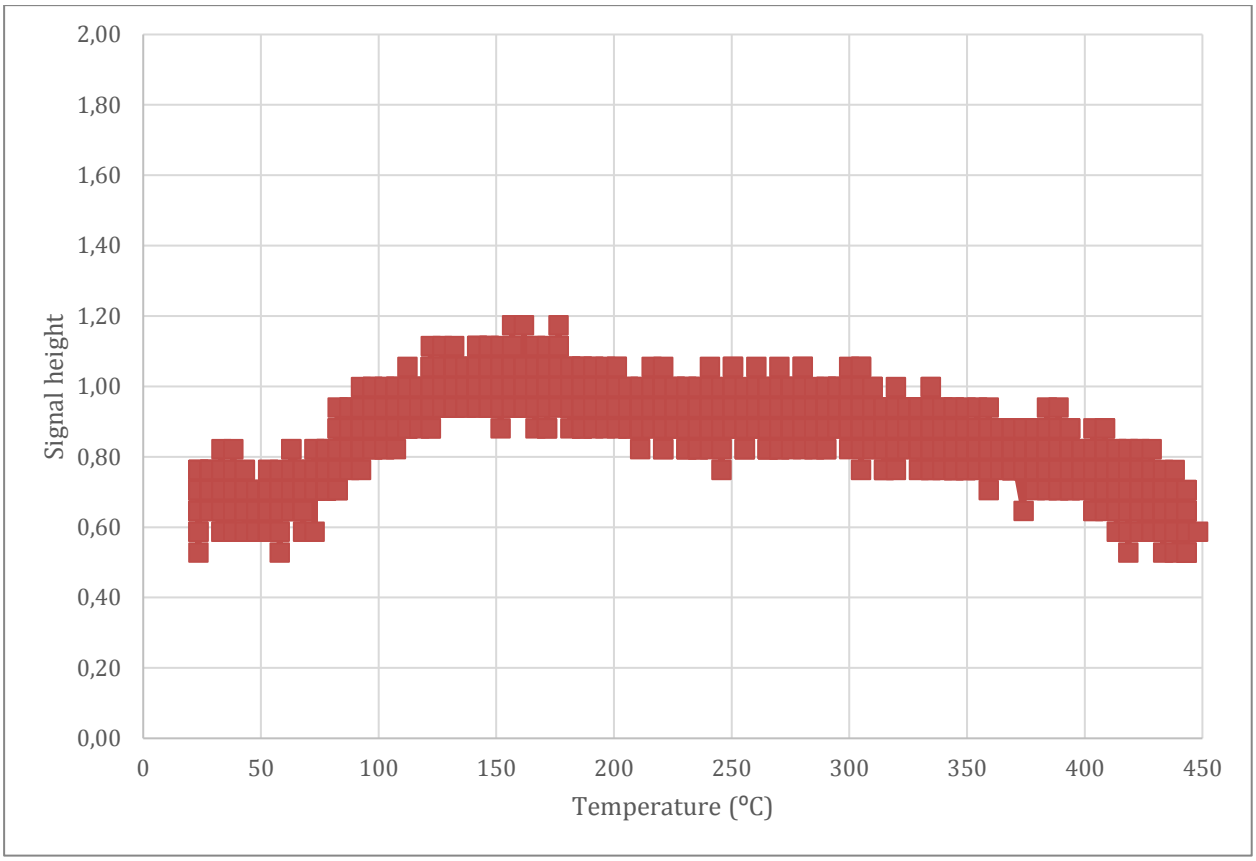

Figure D-2 - Dimensionless signal height on mass 30 (nitric monoxide) over the sample XG6.0M10 with a flowrate100 cm^3/min, NO concentration = 1000 ppm, CO concentration = 1000 ppm and O_2 concentration of 5% (v/v)

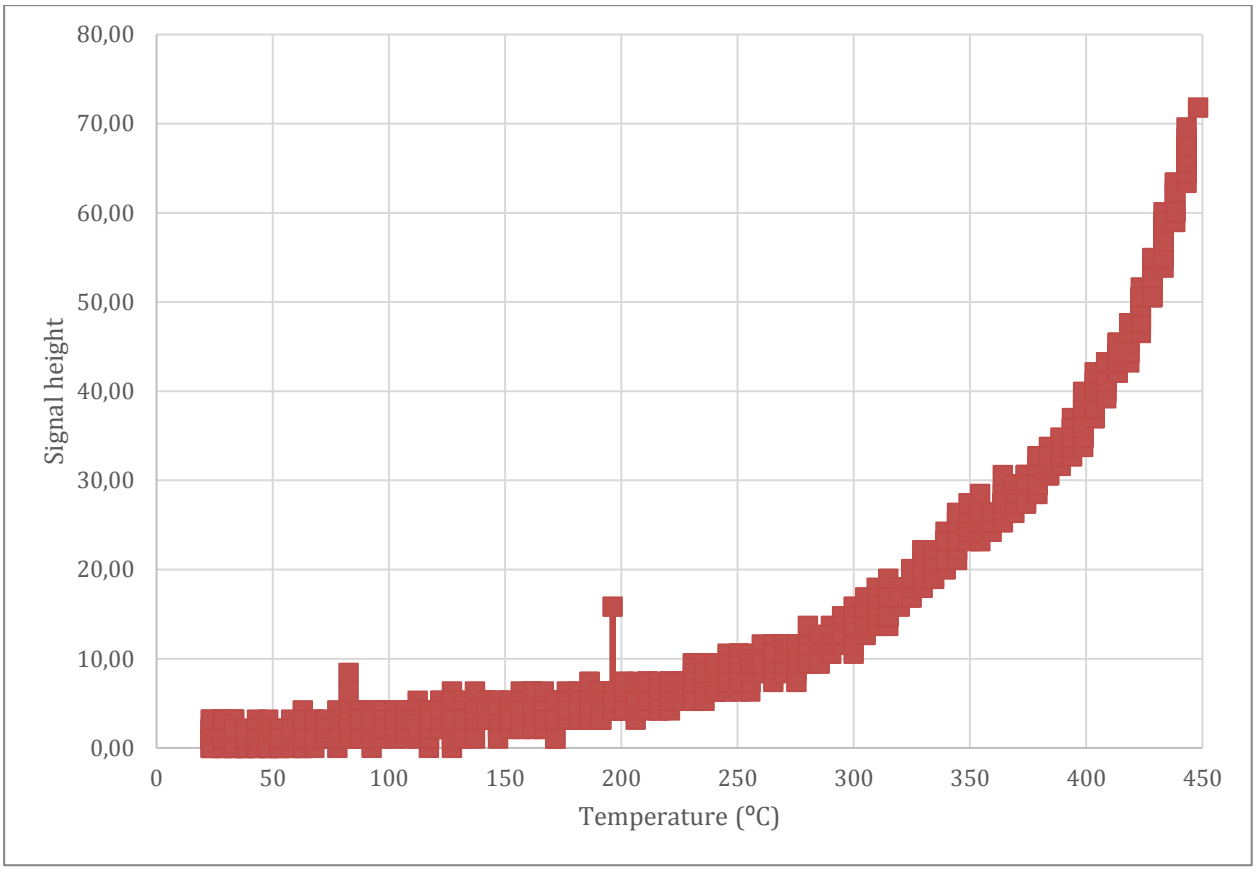

Figure D-3 - Dimensionless signal height on mass 44 (carbon dioxide) over the sample XG6.0M10 with a flowrate100 cm^3/min, NO concentration = 1000 ppm, CO concentration = 1000 ppm and O_2 concentration of 5% (v/v)

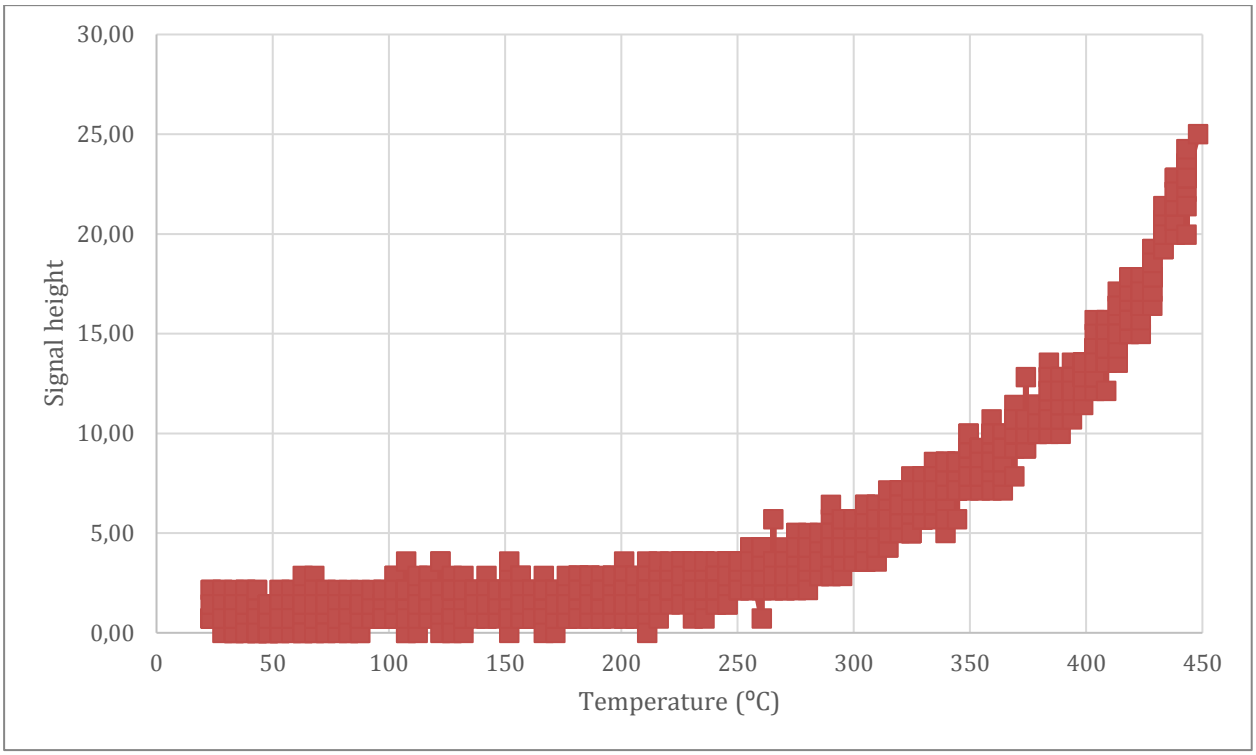

Figure D-4 - Dimensionless signal height on mass 46 (nitric dioxide) over the sample XG6.0M10 with a flowrate100 cm^3/min, NO concentration = 1000 ppm, CO concentration = 1000 ppm and O_2 concentration of 5% (v/v)

Appendix E: Oxygen influence assays

The sample XG5.3aM10 was tested with and without oxygen in order to determine the influence it would have on the catalytic performance. Below, the MS results of these assays are shown. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; CO concentration: 1000 ppm; O_2 concentration (when present): 5% (v/v).

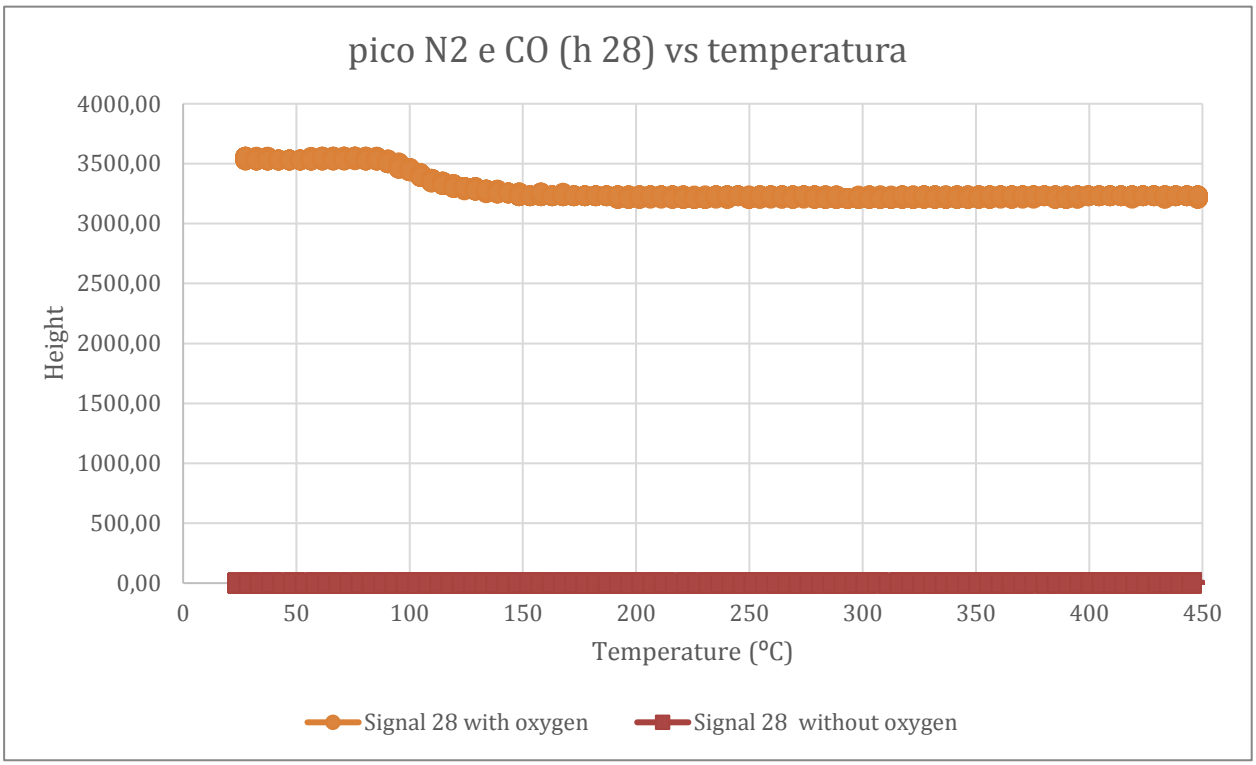

Figure E-1 - *Adimensional signal height on mass 28 (molecular nitrogen and carbon monoxide) on the sample XG5.3aM10. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; CO concentration: 1000 ppm; O_2 concentration (when present): 5% (v/v)*

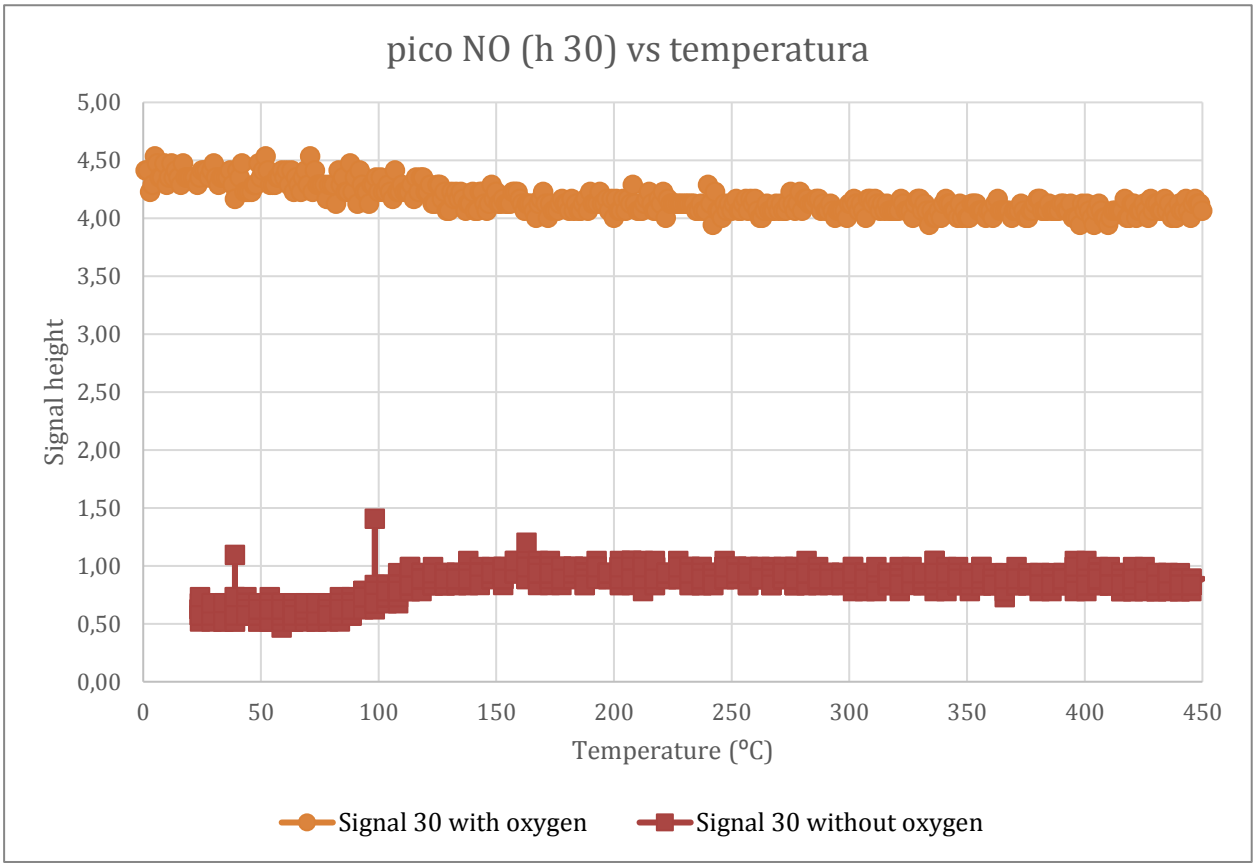

Figure E-2 - *Dimensionless signal height on mass 30 (nitric oxide) on the sample XG5.3aM10. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; CO concentration: 1000 ppm; O_2 concentration (when present): 5% (v/v)*

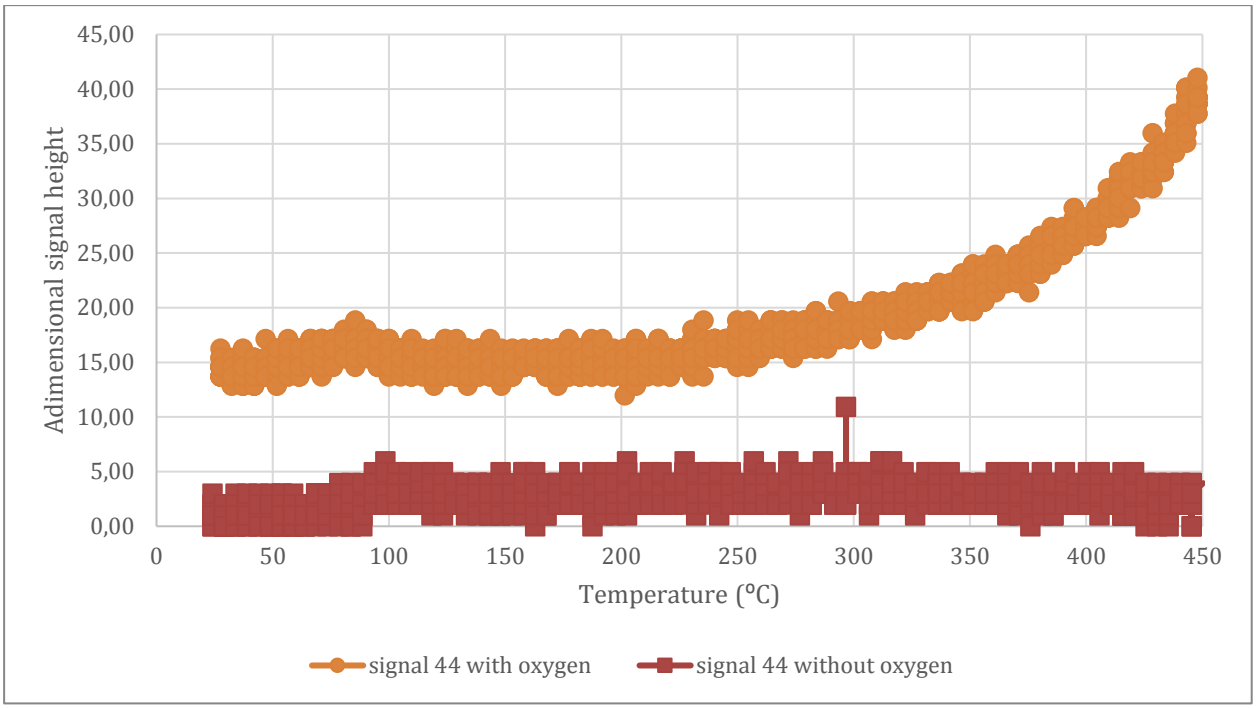

Figure E-3 - *Dimensionless signal height on mass 44 (carbon dioxide) on the sample XG5.3aM10. Flowrate: 100 cm³/min; NO concentration: 1000 ppm; CO concentration: 1000 ppm; O_2 concentration (when present): 5% (v/v)*

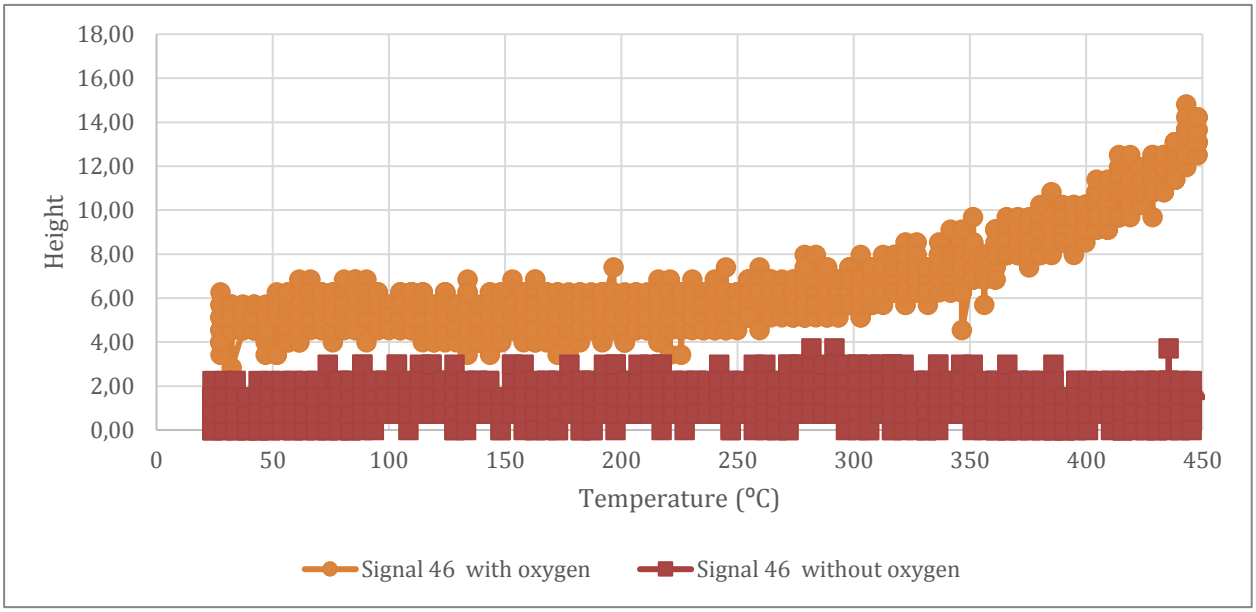

Figure E-4 - *Dimensionless signal height on mass 46 (nitric dioxide) on the sample XG5.3aM10. Flowrate: 100 cm³/min; NO concentration: 1000 ppm; CO concentration: 1000 ppm; O_2 concentration (when present): 5% (v/v)*

Appendix F: Isothermal assay

An isothermal assay was done to test the behaviour of the samples when exposed to 20% O_2 at room temperature. The assay was conducted under a flowrate of 100 cm^3/min; NO concentration: 1000 ppm; O_2 concentration: 20% (v/v). Below, the MS results and the NO/NO_x analyser readings are shown.

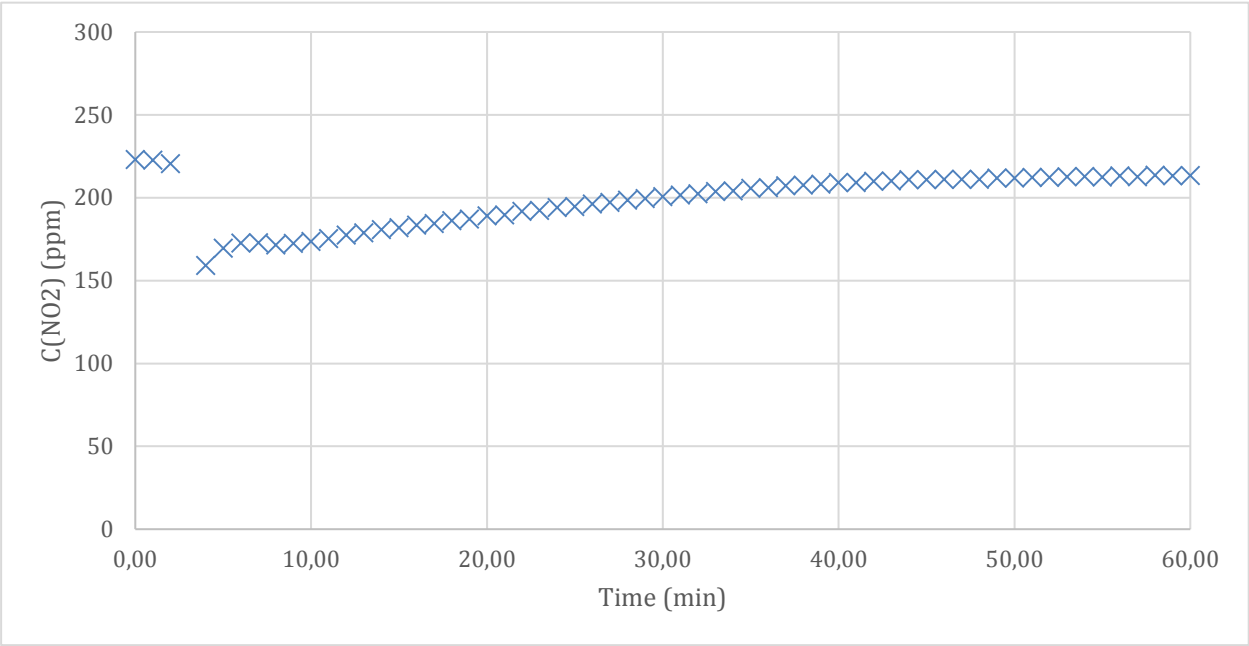

Figure F-1 - Concentration of NO_2 obtained from the sample XG5.3aM10. Flowrate: 100 cm3/min; NO concentration: 1000 ppm; O_2 concentration: 20% (v/v)

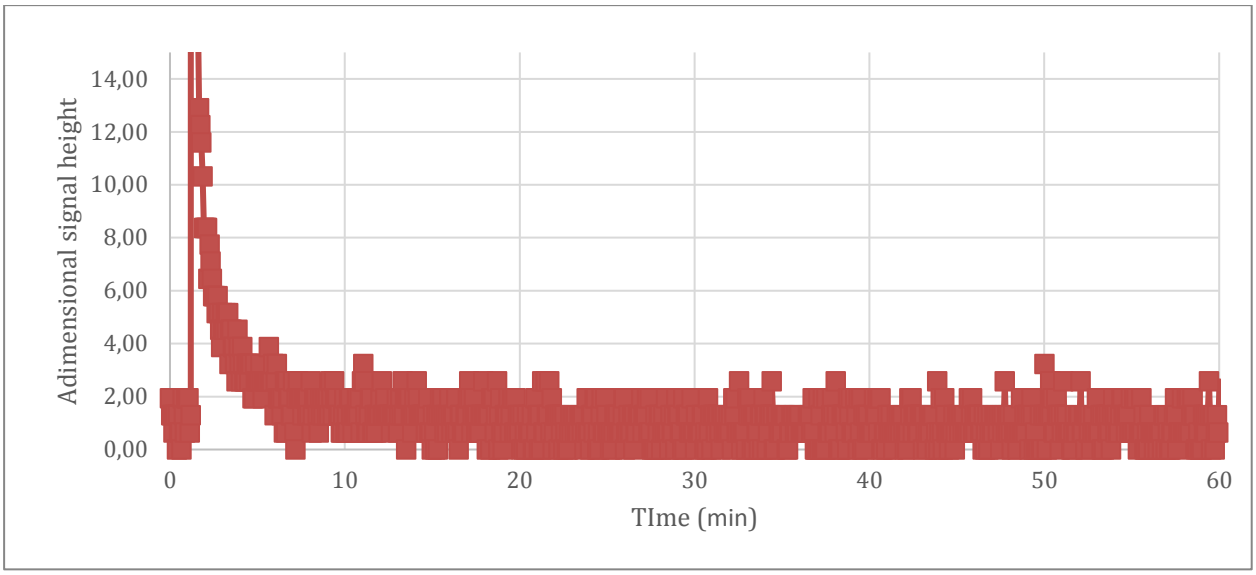

Figure F-2 - *Dimensionless signal height on mass 28 (molecular nitrogen) on the sample XG5.3aM10. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; O_2 concentration: 20% (v/v)*

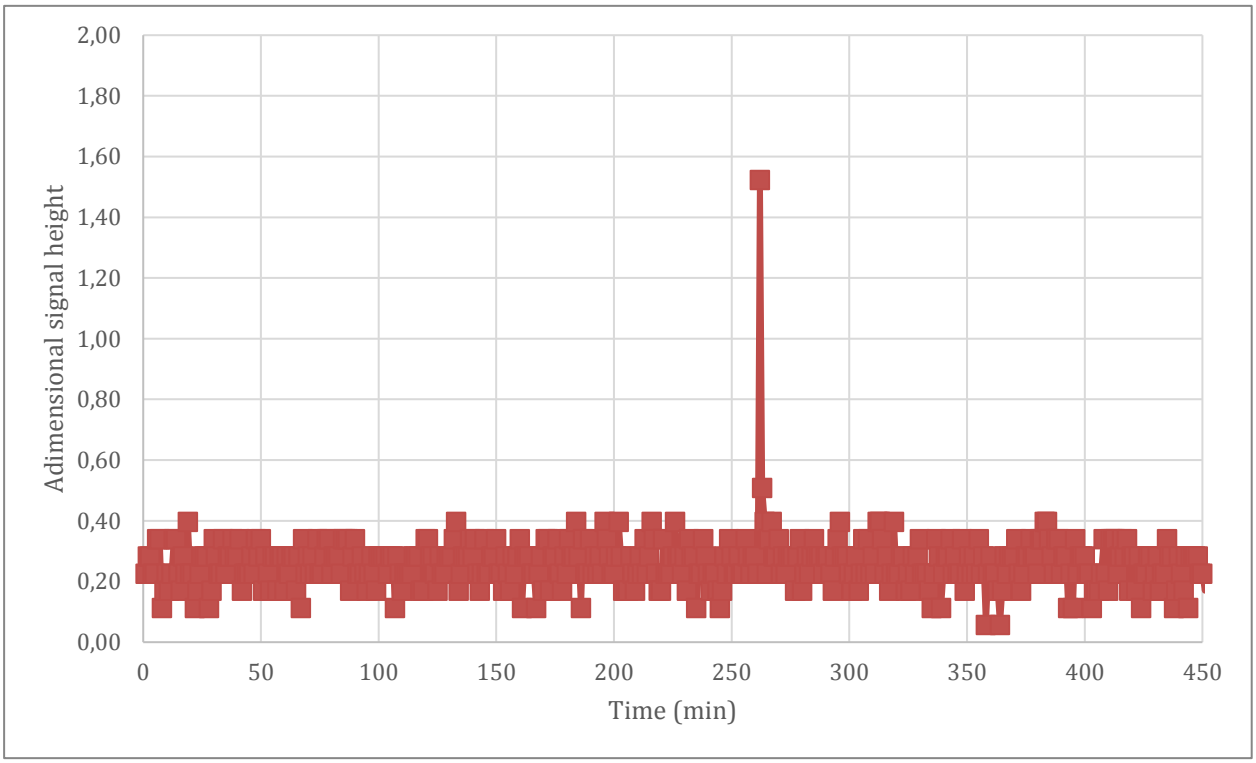

Figure F-3 - *Dimensionless signal height on mass 30 (nitric oxide) on the sample XG5.3aM10. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; O_2 concentration: 20% (v/v)*

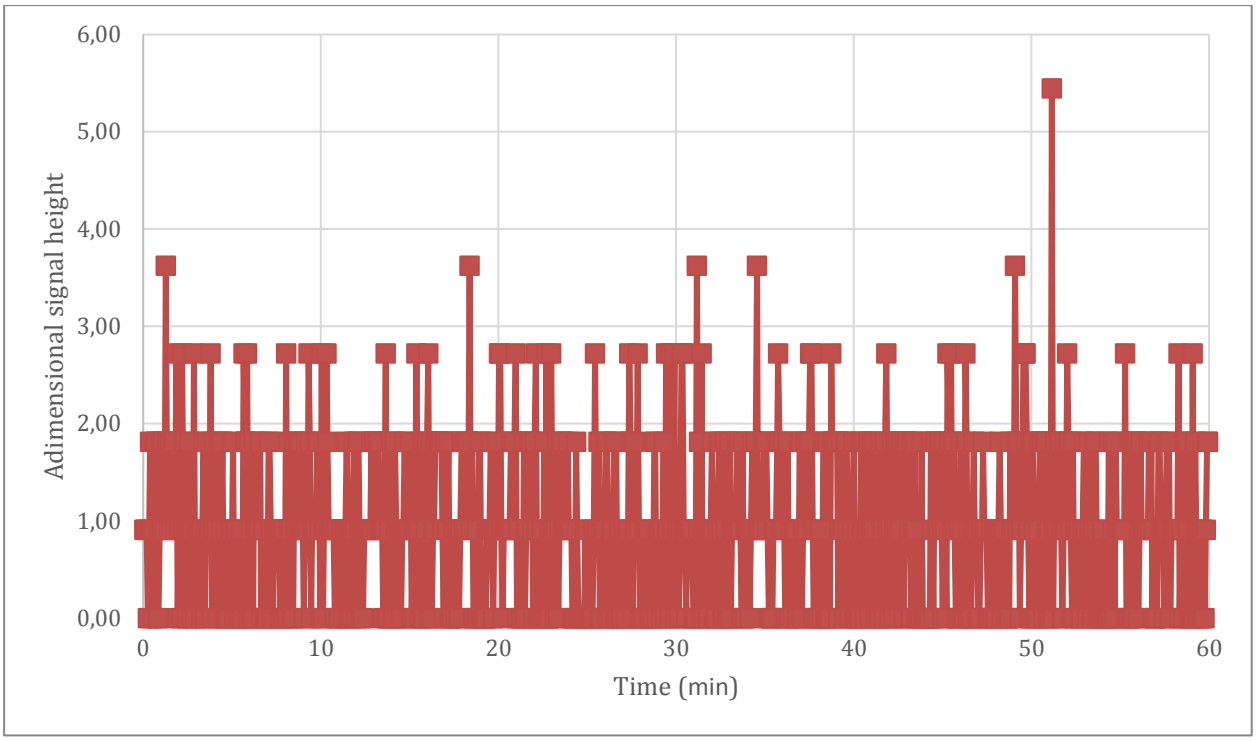

Figure F-4 - *Dimensionless signal height on mass 44 (carbon dioxide) on the sample XG5.3aM10. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; O_2 concentration: 20% (v/v)*

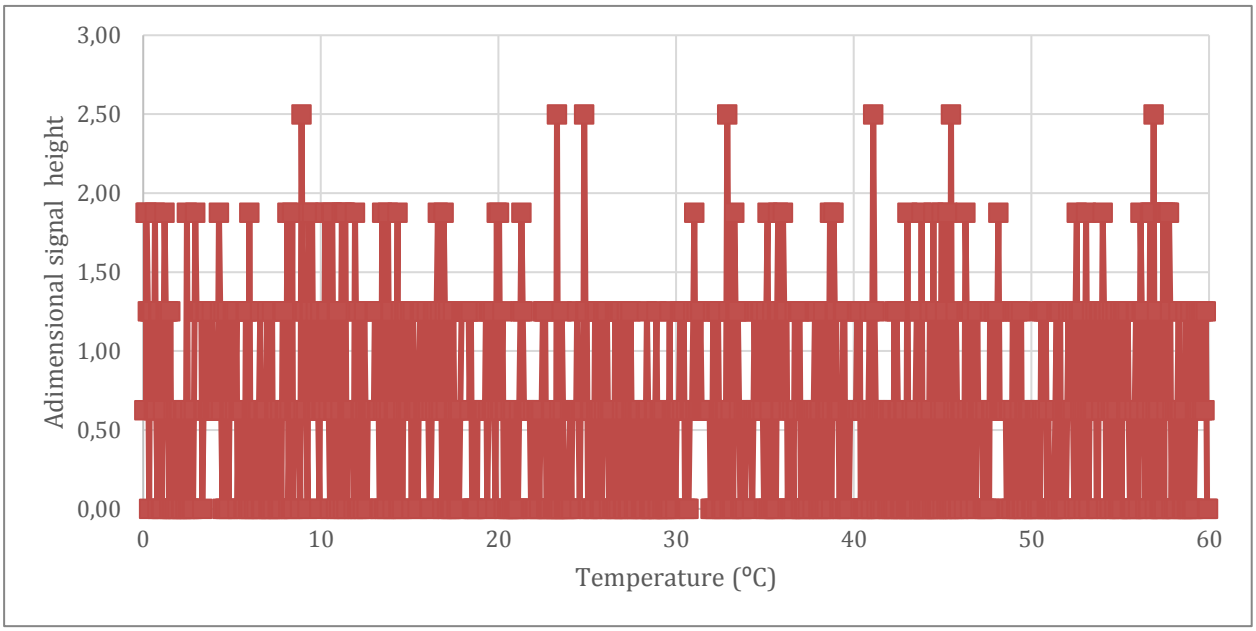

Figure F-5 - *Dimensionless signal height on mass 46 (nitric dioxide) on the sample XG5.3aM10. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; O_2 concentration: 20% (v/v)*

Appendix G: Xerogel assays

Xerogel assays were done to ascertain the influence of the melamine foam in the catalytic performance. The MS results are shown below.

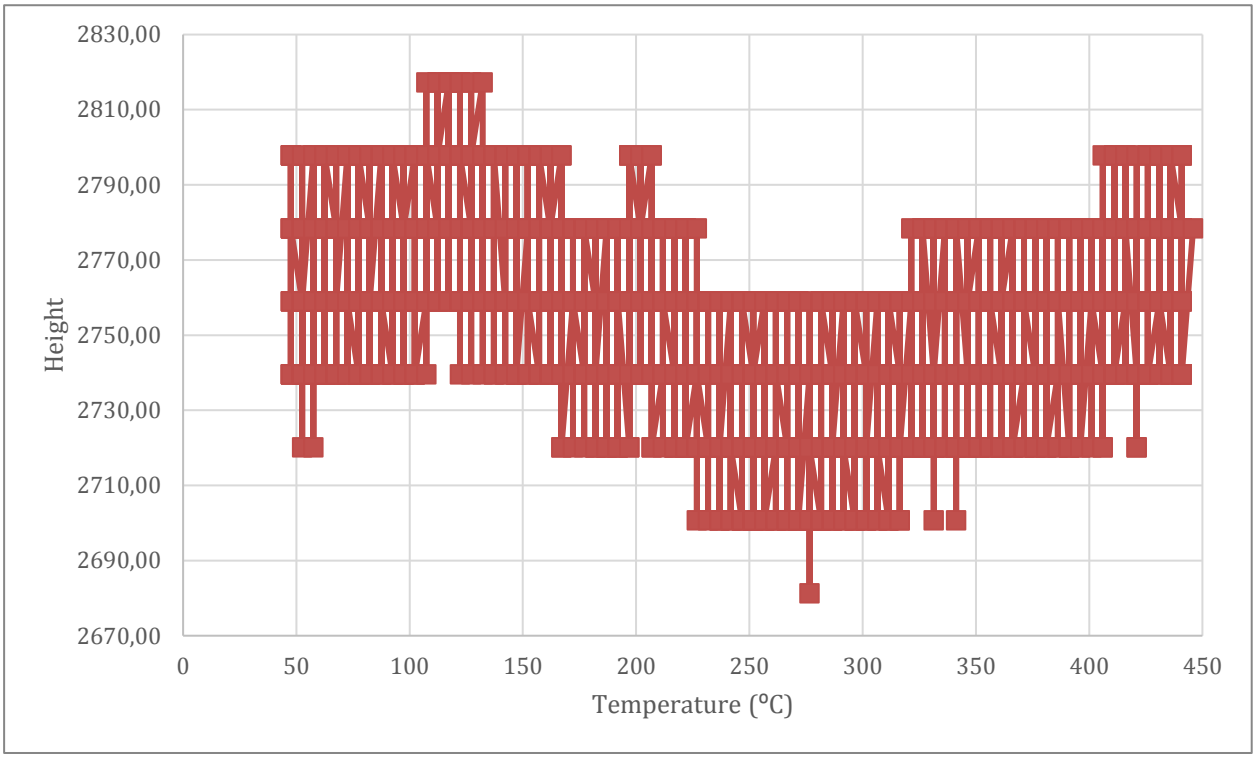

Figure G-1 - *Dimensionless signal height on mass 28 (molecular nitrogen and carbon monoxide) on the xerogel. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; CO concentration: 1000 ppm; O_2 concentration: 5% (v/v)*

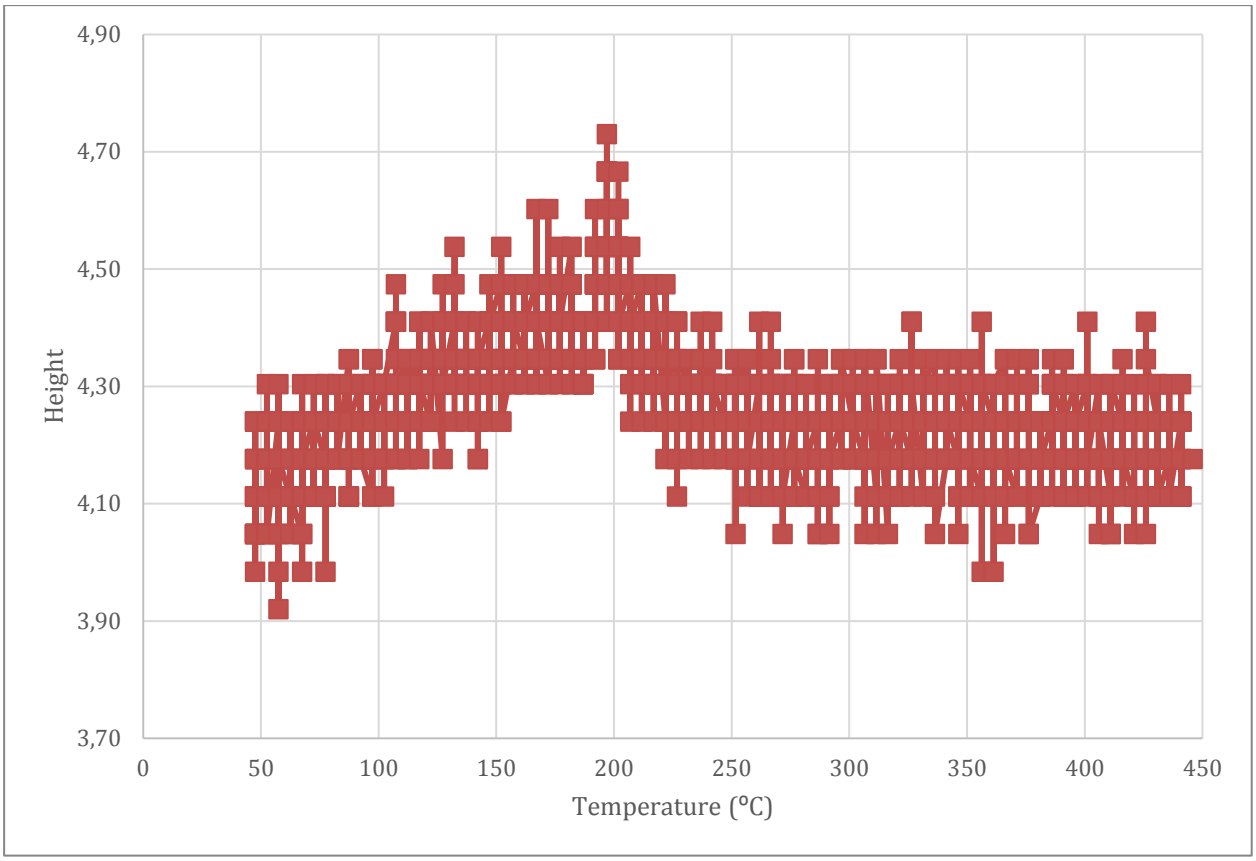

Figure G-2 - *Dimensionless signal height on mass 30 (nitric oxide) on the xerogel. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; CO concentration: 1000 ppm; O_2 concentration: 5% (v/v)*

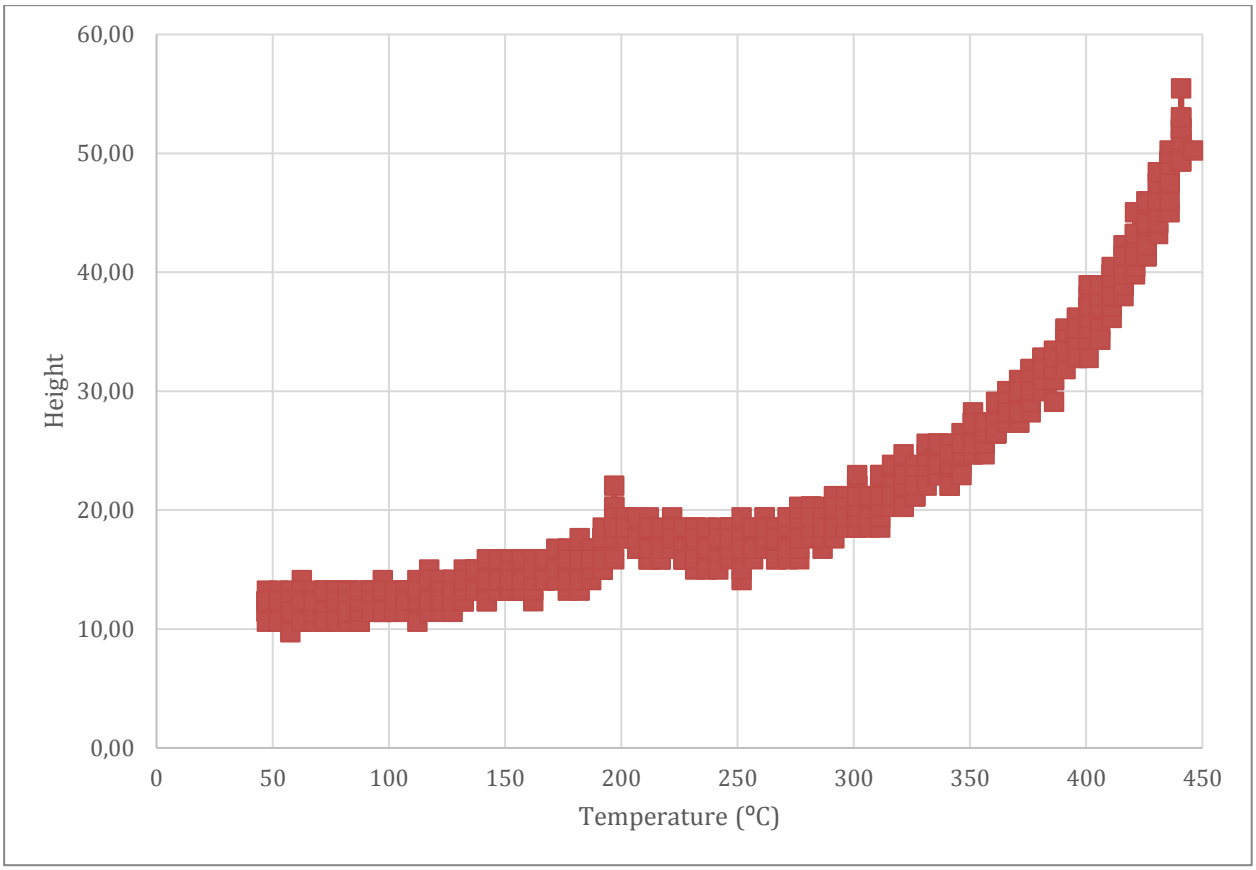

Figure G-3 - *Dimensionless signal height on mass 44 (carbon dioxide) on the xerogel. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; CO concentration: 1000 ppm; O_2 concentration: 5% (v/v)*

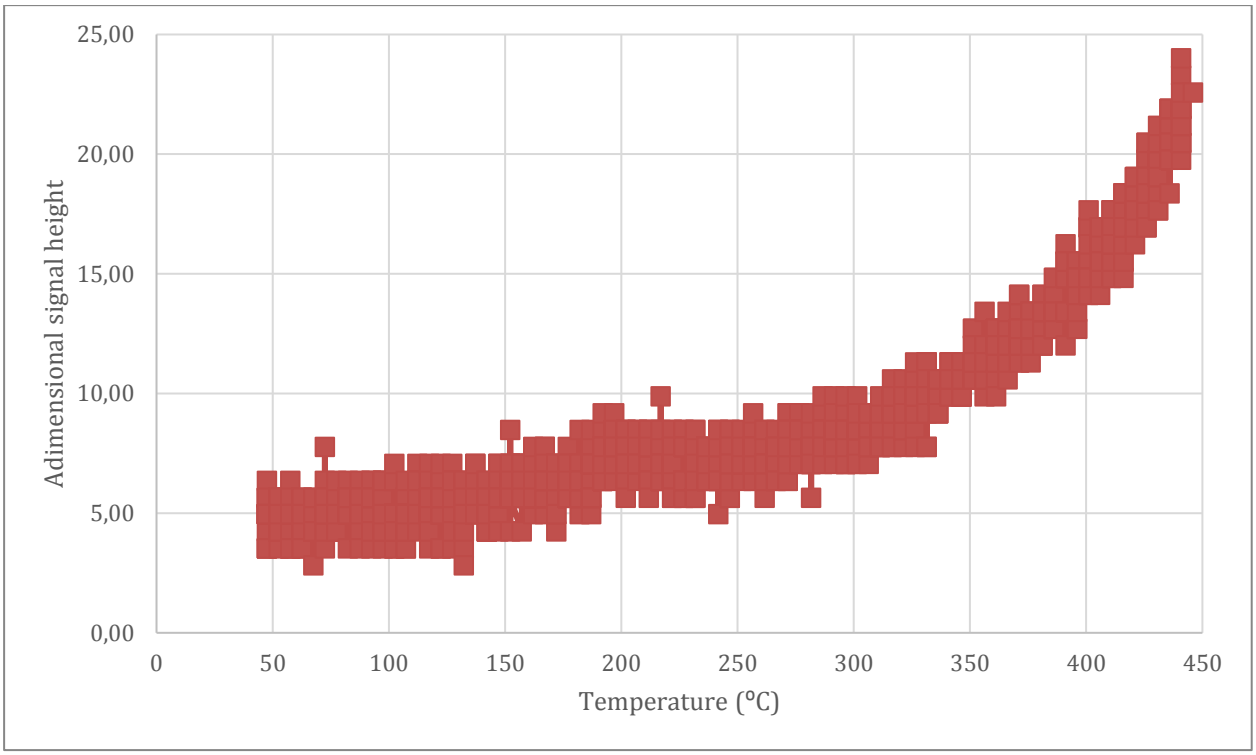

Figure G-4 - *Dimensionless signal height on mass 46 (nitric dioxide) on the xerogel. Flowrate: 100 cm^3/min; NO concentration: 1000 ppm; CO concentration: 1000 ppm; O_2 concentration: 5% (v/v)*

Appendix H: DOE sample selection

DOE methodology was employed in order to plan out the experiments to be carried out in limited time due to pandemic situation. As mentioned before, this methodology was carried out in half-factorial, meaning that 16 samples were chosen. The table below contains those 16 samples.

Sample	Nitrogen precursor	Surfactant inclusion in synthesis	pH	soaking time	Exposure to pressurized air
XG6.0aM2	Melamine	No	6	2	Yes
XG6.0M10	Melamine	No	6.01	10	No
XG5.3M2	Melamine	No	5.30	2	No
XG5.3aM10	Melamine	No	5.30	10	Yes
XG5.3aU2	Urea	No	5.30	2	Yes
XG5.3U10	Urea	No	5.30	10	No
XG6.0U2	Urea	No	6.01	2	No
XG6.0aUS2	Urea	Yes	6.01	2	No
XG6.0US10	Urea	No	6.01	10	Yes
XG6.0aU10	Urea	No	6.01	10	Yes
XG5.3US2	Urea	Yes	5.29	2	No
XG5.3aUS2	Urea	Yes	5.29	2	Yes
XG6.0US10	Urea	Yes	6.0	10	No
XG5.3MS10	Melamine	Yes	5.3	10	No
XG6.0MS2	Melamine	Yes	5.99	2	No
XG6.0aMS2	Melamine	Yes	5.99	2	Yes