Environmental Catalysis and Technologies

Catalytic Technologies for Water and Air Cleaning

Catalytic Oxidation of VOCs

Cryptomelane-type manganese oxide was synthesized by a novel solvent-free technique. A superior catalytic performance in the oxidation of distinct VOCs (90 % conversion of ethyl acetate, ethanol, and toluene into CO_2 achieved at 203°C, 201°C, and 270°C, respectively) was achieved. The powder catalysts were immobilized on ceramic (cordierite) structured supports. The optimized structured catalyst presented high catalytic activity in the removal of ethylacetate (90% conversion into CO_2 at 256 °C) and high stability during 100 h of reaction. Carbon-based catalysts were developed in powder and macrostructured form to be applied in semi-batch and column bubble reactors, respectively, to assess the toluene degradation via heterogeneous Fenton oxidation.

Introduction

Volatile organic compounds (VOCs) are recognized as major contributors to air pollution. These compounds are toxic and can also act as precursors of ground-level ozone and photochemical smog formation. In this context, catalytic oxidation is considered a promising technology for the control of VOC emissions. The most commonly used catalysts for the catalytic oxidation of VOCs are supported noble metals (Pt or Pd), and metal oxides (Co, Cu, Ni, Mn). Mn oxides have the additional advantages of lower cost and higher resistance to deactivation by poisoning compared to supported noble metals. Among Mn oxides, cryptomelane-type manganese oxide (KMn_8O_{16}) was found to be very active during the oxidation of several types of VOCs. The development of fast, simple and low-cost methods to produce highly active catalysts for VOC oxidation is still a challenge, considering that this would require the scaled-up production of various materials.

Current Development

Cryptomelane-type manganese oxide synthesis by a novel solvent-free technique Manganese oxides were synthesized using two new methods, a novel solvent-free reaction and a reflux technique, that produced cryptomelane-type products (K-OMS-2). Mn oxides were also synthesized using conventional methods and all specimens were applied to the oxidation of ethyl acetate and butyl acetate, acting as models for the VOCs found in industrial emissions [1]. The K-OMS-2 nanorods synthesized by the solvent-free method (sample Mn2, Fig.1) showed higher catalytic activity in the ethyl acetate oxidation than K-OMS-2 materials prepared by the reflux technique (sample Mn3, Fig. 1) and than those prepared by the conventional methods (Fig.1). The catalyst with the highest performance also exhibited good stability and allowed 90% conversion of ethyl and butyl acetate to CO_2 at 213 and 202 °C, respectively. The superior performance of the K-OMS-2 catalysts was attributed to the increased average oxidation state of the manganese in these structures.

In the novel synthesis, the grinding step by ball-milling allows the controlled and reproducible synthesis of cryptomelane manganese oxide [2]. Grinding conditions were optimized to ensure a superior catalytic performance in the oxidation of distinct VOCs (90 % conversion of ethyl acetate, ethanol, and toluene into CO_2 achieved at 203 °C, 201 °C, and 270 °C, respectively).

For comparison, a platinum-based catalyst (1%-Pt/Al_2O_3) was also tested and exhibited much lower activities for ester and alcohol; but significantly higher catalytic activity for toluene when compared to the K-OMS-2 catalysts, suggesting that this catalyst is less active for aromatic hydrocarbons. A long-term experiment, using ethanol as a model pollutant, showed that the cryptomelane catalyst was stable for more than 100 h.
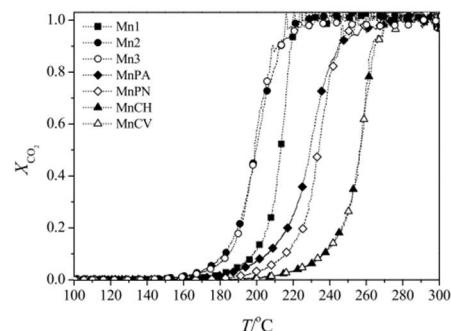

Fig 1. Conversion to CO_2 as a function of temperature during ethyl acetate oxidation [1].

The ability for ion exchange and the mixed valence of manganese of this unique class of inorganic materials offer the opportunity for tuning the physical and chemical properties by the introduction of ions into the tunnels and/or in the framework. The effect of the cation exchange of cryptomelane potassium with other alkali metals (Ce, Li, Na, and Cs) was studied. The influence on physical-chemical properties and catalytic performance was evaluated for the catalytic oxidation of ethyl acetate, ethanol, toluene and acetone. The most active catalyst in the oxidation of ethyl acetate, ethanol and acetone studied was KOMS_Cs, while in the case of toluene, it was KOMS_Ce. Both specific surface area and the average oxidation state of the manganese species present in the catalyst seem to positively influence the performance of the materials. Finally, the KOMS_Cs catalyst was studied in a simulated system of mixtures of the VOCs under study, verifying the total oxidation into CO_2 of all compounds at a temperature below 250 °C.

Macrostructured supported cryptomelane-type manganese oxides The immobilization of powder catalysts on structured supports, like a monolith, can bring numerous advantages such as low-pressure drop (which allows lower energy consumption), high catalytic performance per mass of active phase, high specific surface area, good interphase mass transfer (due to the very thin catalyst layer), and a much easier separation and cleaning. Ceramic (cordierite) and metallic (FeCrAlloy®) monoliths coated with K-OMS-2 were prepared and tested as catalysts for the oxidation of ethyl acetate (Fig.2) [3]. Monoliths with different cell sizes, prepared with the same number of immersions in the wash coating solution or with similar loadings, were tested to evaluate the effect of this parameter on the adherence of the active phase and the catalytic activity of the final monolith. The adherence of the coating was high, with less than 5% weight loss after the ultrasound test. The ceramic monolith presented the highest activity, achieving 90% conversion to CO_2 at 227 °C, between 10 and 77 °C less than the metallic. These results could be

related to the thermal behavior of these monoliths, due to their different thermal conductivities. Further optimization of the preparation conditions of cordierite honeycomb monoliths was made, with several coating parameters being studied. The
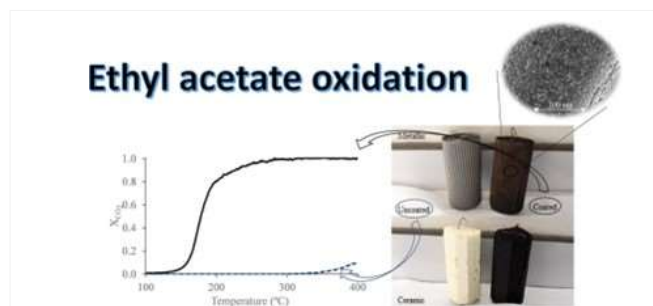

Fig 2. Conversion of ethyl acetate into CO_2 over the ceramic and metallic monoliths coated with cryptomelane-type manganese oxides [3].

presence of an initial coating with alumina and a binding agent (colloidal alumina) in the wash coating solution was found essential to increase the activity, whereas increasing the calcination temperature after the initial alumina coating above 500 °C decreased the catalyst activity. The optimized structured catalyst presented high catalytic activity in the removal of ethyl acetate (90% conversion into CO_2 at 256 °C) and high stability during 100 h of reaction. The addition of toluene or water vapor in the feed gas did not significantly affect the coated monolith activity [4].

In collaboration with CeNTI – Centre for Nanotechnology and Smart Materials a Master thesis was carried out with the aim to develop a new and innovative filtration systems for pollutant emissions using baghouse filters. For this purpose, the supported and unsupported Mn-based powder catalysts were prepared and formulations for their incorporation into textile-based substrate were studied. Ethyl acetate was used as VOC model molecule to evaluate the substrates performance. The most promising catalytic system (a impregnated PTFE felt), achieved the conversion of 90 % of ethyl acetate into CO_2 at 225 ºC, and during the stability test, the catalyst system remained stable. The results obtained were very promising, since there was no deactivation during the time studied, and the conversion of ethyl acetate into CO_2 remained close to 90%.

Metal Zeolite Catalysts The presence of two metals (M^1M^2) in a zeolite structure enhances the degradation of pollutants in the liquid or gas phase compared to monometallic catalysts. In collaboration with the Chemistry Centre of the University of Minho, the catalytic oxidation of ethyl acetate in the gas phase was studied over metal zeolite catalysts based on NaY prepared by the ion-exchange method [5]. The metal zeolite catalysts were optimized by using several parameters: (i) the presence of a second metal in M^1M^2 catalysts; (ii) the presence or not of a noble metal in the pair CuM^2 (M^2=Pd, Zn or Ag); (iii) the order of introduction of the metals in M^1M^2 catalysts (CuPd or PdCu); (iv) particle size of NaY and NaY nano; and (v) the effect of simultaneously adding metal species (Cu and Pd). M^1M^2 catalysts presented the best results compared to the monometallic catalysts, and the presence of a noble metal in M^1M^2 catalysts enhanced their activity. Among the metal phases studied, the catalyst (CuPd)0.01-Y has shown to be the most efficient due to the interaction between the zeolite lattice and the metal cations. The presence of Pd remarkably increases the performance, allowing a 90% oxidation of ethyl acetate into CO_2 under 300 ºC.

Metal-Carbon Catalysts A novel approach for treatmenting VOCs from gaseous streams was developed in collaboration with the Group of Prof. Luis Miguel Madeira from LEPABE. For that, activated carbon-based catalysts (metal-free or iron-impregnated) with different textural and chemical surface properties and a semi-batch bubble reactor were used, aiming to assess the toluene degradation via heterogeneous Fenton oxidation [6]. The materials' chemical surface properties, particularly the presence of N-surface groups, were herein found to play an important role in toluene adsorption and catalytic performance. The maximum amount of toluene transferred, 6.39×10^{-3} mol, was achieved using melamine-doped activated carbon that was impregnated with iron (ACM-Fe). This iron-based catalyst was found to be quite stable during 3 reutilization cycles. Moreover, the degradation of toluene (present in a gas stream) was also evaluated in a bubble column reactor by this process, using macrostructured carbon-coated monolith catalysts synthesized by chemical vapor deposition (CVD), which allowed carbon growth in honeycomb cordierite monoliths, while the iron (metal phase) was incorporated by adsorption [7]. A detailed parametric study was carried out to evaluate the effect of the main variables and process operating conditions. The maximum ratio between the toluene transferred per catalysts mass - η/W - (6.78×10^{-2} $mol_{toluene}$ g_{cat}^{-1}), with total oxidant consumption and lower intermediate compounds remaining in solution (DOC = 33 mgC dm^{-3}), was reached when the process was performed with a monolith with a channel density of 230 cpsi, initial pH = 3.0, [catalyst] = 0.8 g dm^{-3}, [H_2O_2] = 20 mmol dm^{-3}. During all experiments, only a small amount of iron was leached from the catalyst to the liquid phase (ca. <1.0 wt.%), proving its stability for this application.

Future Work

Immobilization studies of powder catalysts into macrostructured supports (or substracts) are required to overcome the decreased catalytic performance when compared with the powder catalysts. It is relevant to study simulated mixing systems with other combinations of compounds in the presence of water vapour, to study the possible phenomena of competition between pollutants in real industrial effluents.

Related Sustainable Development Goals

Outputs

PhD Theses
Diogo F.M. Santos, *Development of structured catalysts for pollution control*, PDEQB, FEUP, 2019.

Master Dissertations
Débora O. Pereira, *Imobilização de sistemas catalíticos em substratos de base têxtil para tratamento de efluentes gasosos*, MIEA, FEUP, 2018.
Maria M.C. Fonseca, *Oxidação catalítica de compostos orgânicos voláteis*, MIEA, FEUP, 2023.

Selected Publications
[1] O.S.G.P. Soares et al., Chinese Journal of Catalysis, 39, 27, 201836, (2018).
[2] D.F.M. Santos et al., Environmental Technology, 10, (2018).
[3] D.F.M. Santos et al., Chemical Engineering Journal 382, 122923 (2020).
[4] D.F.M. Santos et al., Environmental Technology 42, 16, 2504 (2021).
[5] O.S.G.P. Soares et al., ChemCatChem, 10, 3754-3760 (2018).
[6] Sampaio, E.F.S., et al. Nanomaterials, 2022, 12(19), 3274
[7] Sampaio, E.F.S., et al. Catalysis Today, 2023, 418, 114143

Team
José L. Figueiredo Emeritus Professor; M. Fernando R. Pereira, Full Professor, Group Leader; José J.M. Órfão, retired Associate Professor; O. Salomé G.P. Soares, Auxiliar Researcher; **Raquel P. Rocha**, Contract researcher; Diogo F.M. Santos, former PhD Student, **Emanuel F.S. Sampaio**, PhD Student.

Funding

Catalytic Technologies for Water and Air Cleaning

Integrated Catalytic Processes for Water Treatment

The integration of catalytic ozonation and catalytic reduction was studied as a strategy to perform the simultaneous removal of organic and inorganic pollutants present in water.

The study of the integration of both techniques was performed in *batch* reactions allowing to conclude that the presence of organic matter significantly reduces the conversion of inorganic species, leading to catalyst deativation due to organic matter adsorption on the metallic active centers. This deactivation could be overcome by the use of bimetallic catalysts with higher metal content (5%Pd-2.5%Cu).

Additionally, the combination of catalytic ozonation and reduction of halogenated organic compounds was very efficient, since the application of these processes allows the degradation of the organic molecule and the breakage of the strong C-halogen bond.

Introduction

Fulfilling the demands for drinking water and wastewater treatment has become a major social, technological, economic, and political priority. With the increasing deterioration of water quality over the past few years, efforts have been made to develop new efficient technologies for water treatment. One of the greatest challenges faced by wastewater treatment facilities is related to the complexity of the matrices (different types of pollutants present), requiring different processes and a combination of different technologies.

Oxidation processes, such as ozonation, are a well-developed class of technologies widely used in water and wastewater treatment for disinfection and degradation of toxic organic pollutants. To achieve a higher organic matter mineralization degree, it is usual to combine this process with other oxidant substances, radiation, or a solid catalyst to promote O_3 decomposition into hydroxyl radicals (OH•) that will actively participate in the organic matter degradation. However, inorganic compounds may be released into solution during the degradation of organic matter and persist after these processes, requiring the application of an alternative technique for their removal.

Inorganic species, such as nitrate (NO_3^-) and bromate (BrO_3^-), are some of the species that raise more concern about their presence in water for human consumption due to the associated harmful effects.

From an ecological point of view, it is related to the pollutants conversion into less toxic species. This way, catalytic reduction in the presence of supported metallic catalysts emerges as an efficient approach to perform the treatment of water contaminated with inorganic species, allowing to convert them into less toxic species (N_2 and Br^-)

Moreover, halogenated organic compounds, namely 4-chlorophenol (4-CP) and 4-fluorophenol (4-FP), pose significant environmental risks due to their high stability. Catalytic hydrodehalogenation (CHD) emerged as a technique to address contamination, and palladium-based catalysts have been shown to be effective in degrading these types of contaminants.

In order to give an answer to the present problematic, the possibility of integrating catalytic ozonation and catalytic reduction treatments to perform the simultaneous removal of organic and inorganic species (respectively) was acutely studied.

Current Development

Ozonation/catalytic ozonation reactions were performed using model organic pollutants (4-Nitrobenzaldehyde, 4-NBA and Ampicillin, AMP) susceptible to forming N- inorganic species (mainly NO_3^-) after treatment. To complete the treatment process, a catalytic reduction reaction was perfomed using supported metallic catalysts.

Special attention was directed to the application of palladium-copper catalysts (Pd-Cu) synthesized on different supports, for both NO_3^- and BrO_3^- conversion. This proved to be one of the most efficient combinations to perform an adequate conversion of both oxyanions with a good selectivity to the formation of less toxic species (N_2 and Br^-, respectively) [1]. When applied in the treatment of simulated solutions (only with the oxyanions present in water) conversion values of 100 % were achieved for Pd-Cu catalysts supported on CNT, TiO_2 and composite materials of CNT and TiO_2; however, the selectivity obtained for NO_3^- conversion process would be deprioritized when using a metal oxide as a support.

The synthesized catalysts were studied for the treatment of after ozonation solutions, with organic matter present. The conducted studies (Fig 1 (A)) showed an increasingly negative influence in NO_3^- conversion with the presence of organic matter in solution, conducting to the catalyst deactivation. This negative influence was not so evident for BrO_3^- conversion due to the lower complexity of the process (direct conversion of BrO_3^- into Br^- in the noble active centers) allowing to conclude that the deactivation of the catalyst may be associated with a complexation of the organic matter in solution with the copper metal centers (inhibiting the NO_3^- adsorption step on Cu centers) (Fig 1 (B) and (C)). [2].
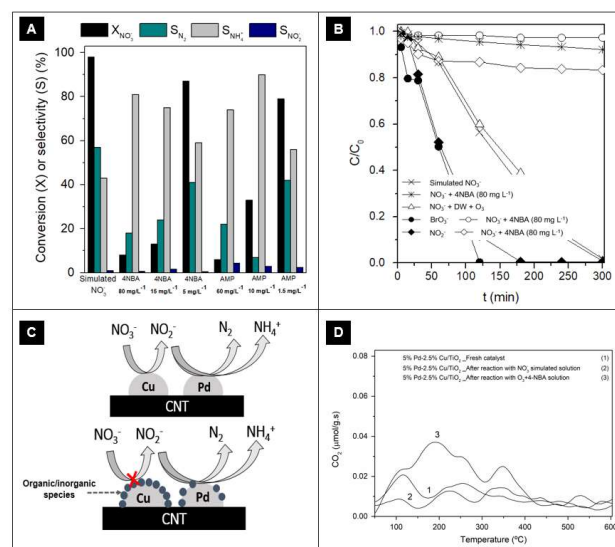

Fig 1. NO3- conversion and selectivities (in %) into NO2-, NH4+ and N2 after 300 min of reaction with 1%Pd-1%Cu/CNT (A), results obtained for NO3-, BrO3- and NO2- in different matrixes (B), schematic representation of the possible reaction mechanism for NO3- reduction in the presence of organic matter (C) and TPO profiles regarding CO2 evolution obtained for fresh and used catalysts (D).

The performed studies showed that the catalyst deactivation may be associated with organic matter adsorption on active sites of the bimetallic catalyst; the catalyst was found to be active for NO_2^- and BrO_3^- reduction, in the presence of organic matter, meaning that palladium centers of the bimetallic catalyst are at least partially available to participate in the reaction (Fig 1 (B)). TPO experiments, performed on fresh and used bimetallic catalysts, allowed to conclude the existence of organic matter adsorption on the metal active centers (Fig 1 (D)). The used catalyst was susceptible to being regenerated through a calcination/reduction thermal treatment, allowing the recovering of the initial activity of the catalyst.

Optimized immobilization and impregnation techniques were applied to perform the incorporation of the most efficient powder catalysts in a macrostructured support (cordierite monolith). The synthesized bimetallic macrostructured catalysts were tested for the continuous conversion of NO_3^- and BrO_3^- present in solution. Promising results were achieved for the continuous treatment of water contaminated with different oxyanions (special attention was directed to NO_3^- and BrO_3^- conversion) (Fig 2). However, some optimization regarding the used catalysts is still needed to achieve higher conversion results with adequate selectivities (to avoid the formation of toxic inorganic by-products) [3,4]. The most efficient results were obtained while implementing the optimized reaction conditions, in a continuous operating system [5].
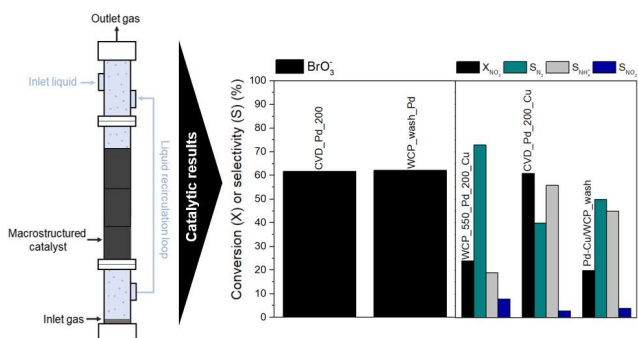
Fig 2. NO3- and BrO3- conversion results obtained after treatment in a continuous catalytic system using immobilized catalyst.

Palladium-based catalysts were synthesized using both carbon materials and metal oxides to be applied in the catalytic hydrodehalogenation reaction, and the pH influence was also studied. For 4-CP degradation, the 5% Pd/CNT BM catalyst showed superior performance in water, while the 5% Pd/TiO_2 catalyst exhibited the fastest degradation in a 2 mM NaOH solution, and all catalysts demonstrated complete C-Cl bond breakage (Fig 3). Reusability tests revealed that the catalyst was not deactivated in a 2 mM NaOH solution, but a decline in catalytic activity was observed in water, probably due to HCl poisoning. Low conversion values were observed for the hydrogenation of 4-FP, leading to the adoption of the catalytic ozone method, which yielded improved results. Similarly, the breakage of C-F bond was complete.

Future Work

As future work on the present research topic, an integrated catalytic system, focused on the integration of catalytic ozonation and reduction processes, has been developed with the objective of performing the simultaneous treatment of organic and inorganic species present in water. Further studies to prove the viability of the idea are still being performed.

Per- and polyfluoroalkyl substances (PFAS), also known as the Forever Chemicals, are compounds that comprise a variable-length carbon chain where hydrogen atoms, or all of them, in nonfluorinated substances bound to the chain, are

replaced by fluorine atoms. Therefore, the complete breakage of C-Cl and C-F bonds was observed in the study of halogenated organic compounds, suggesting that this methodology is ideal for degrading PFAS, which are known to hardly degrade in the natural environment.
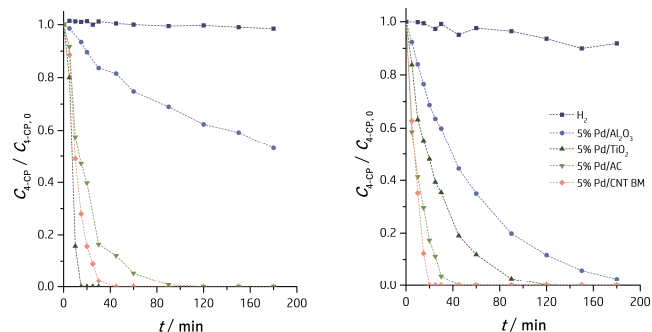
Fig 3. Normalized concentration profile of 4-CP ($C_{4-CP}/C_{4-CP,0}$) during HDC reaction in 2 mM NaOH solution (a) and in water (b).

Related Sustainable Development Goals

Outputs

Patents

O. Salomé Soares, Carla Orge, João Restivo, M. Fernando Pereira, A. Sofia Santos, Integrated catalytic system for the simultaneous removal of organic and inorganic pollutants in drinking water treatment plants, 2023.

Selected Publications

[1] A.S.G.G. Santos, et al., C. 6 (2020) 78.
[2] A.S.G.G. Santos, et al., J. Environ. Chem. Eng. 9 (2021) 105545.
[3] A.S.G.G. Santos, et al., Environ. Technol. (2022).
[4] A.S.G.G. Santos, et al., Appl. Catal. A Gen. 643 (2022) 118790.
[5] A.S.G.G. Santos, et al., Processes. 11 (2023) 2692.

Team

M. Fernando R. Pereira, Full Professor**;** José J.M. Órfão, Retired Professor**; O. Salomé G. P. Soares,** Associate Researcher, **Carla A. Orge,** Contract Researcher**; João Restivo, former** Contract Researcher; **A.Sofia G. G. Santos,** PhD student; **João M. C. B. Costa**, former Project Researcher; **Catarina Lopes,** Project Researcher.

Funding

Nanostructured Carbon Materials

Catalytic Technologies for Water and Air Cleaning

DeNOx technologies

The selective catalytic reduction of NOx with carbon (SCR-C) is an alternative technology to the more common reduction processes using NH₃ (SCR-NH₃). Carbon materials are relatively inexpensive, providing a great alternative to traditional catalysts. The presence of a metal in the structure of different carbon materials (Activated Carbon, Carbon Nanotubes and Carbon Xerogel) is essential for the NOx reduction. Surface chemistry plays an important role in the performance of carbon materials in controlling NOx emissions, particularly nitrogen groups, which are considered to have a promoting effect on NOx removal.

Introduction

Pollution is one of the problems with a significant impact in the 21st century caused by excessive human consumption, directly affecting the climate, the quality of drinking water, agricultural production and, consequently, the health of living beings. Nitrogen oxides (NOx) are considered one of the pollutants that cause the most concern in terms of atmospheric contamination and several measures have been applied to reduce their emissions, essentially in the chemical and transport industries, to prevent these gases from being emitted into the atmosphere. Existing processes for eliminating NOx, in addition to presenting many problems, use expensive catalysts, which makes their commercialization difficult.

Carbon-based catalysts are promising for SCR-C. The C-NO reaction leads to the formation of N₂, CO and CO₂, as shown in equations 1 and 2:

$$2NO + C \rightarrow N_2 + CO_2 \quad (1)$$
$$2NO + 2C \rightarrow N_2 + 2CO \quad (2)$$

The use of carbon in SCR makes the process more economical. The carbon matrix acts both as a catalyst or catalyst support and as a reducing agent. Carbon materials are widely used in catalysis due to their high specific surface area and well-developed pore structure.

To further improve the reactivity of carbon to NOx reduction, transition metals (Cu, Ni, Fe) and alkali metals (K) have been reported as catalysts, increasing the NOₓ adsorption capacity on carbon materials and decreasing the activation energy of NOₓ reduction. It has also been found that potassium can significantly alter the reactivity of carbon during NOx reduction. Furthermore, the application of metal composite catalysts has also been reported.

Recently, there has been increasing interest in nitrogen-doped carbon materials. N-doping of carbon materials increases the surface electron density and the ability to donate them, which results in better catalytic performances.

This research topic aims to explore the potential of catalysts in controlling NOₓ emissions through the preparation and functionalization of carbon materials with controlled physicochemical properties (texture and surface chemistry), as well as the preparation of structured catalysts, which represent an alternative attractive to conventional powder catalysts due to their better heat and mass transfer, reduced pressure drop and superior thermal and mechanical stability.

Current Development

NO reduction: powder catalysts

Carbon materials (activated carbons and carbon nanotubes) were subjected to a series of treatments aiming at the introduction of oxygen and nitrogen surface groups, which were fully characterized by different techniques to evaluate their surface properties. Carbon xerogels were subsequently prepared, in which nitrogen functional groups were introduced during the synthesis process. Nitrogen-free carbon xerogels were also prepared to evaluate the effect of nitrogen on the catalytic activity of carbon materials.

Carbon materials alone were applied to reduce NOx, and under the conditions tested, it was found that they do not present significant catalytic activity. The introduction of the oxygen and nitrogen surface groups slightly improved the catalytic performance; the N-doped catalyst showed the best performance for the NO reduction.

The incorporation of a metal significantly increased the catalytic activity of carbon materials in reducing NO (Fig 1. (a)) AC@5Cu showed a NO conversion of 50%, which increased to 82% for AC@10Cu. However, NO conversion decreases when introducing 15 wt% or 20 wt% Cu. The copper content influences the catalytic activity, with 10 wt% by weight showing the best performance. This maximum may be associated with the active phase dispersion and the metal/support area [1].
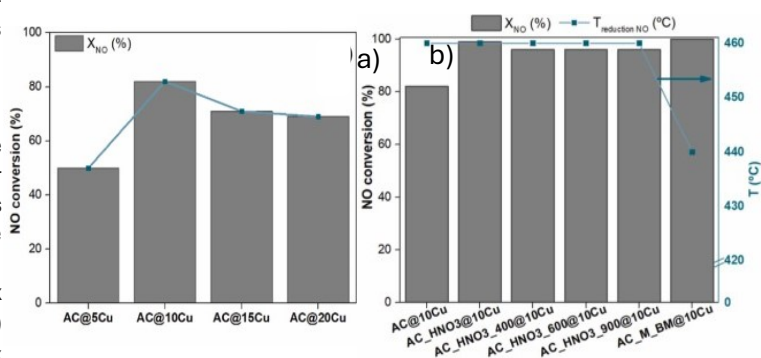

Fig. 1 NO conversion and temperature to reach full conversion in the presence of Cu-based catalysts. (a) effect of metal content (b), effect of functionalized carbon supports.

Fig. 1 (b) shows that Cu-based catalysts on functionalized supports show higher conversions than pure activated carbon impregnated with Cu. The AC_M_BM@10Cu sample showed complete conversion at 440 °C, while the AC_HNO₃@10Cu sample showed 99% conversion only at the end of the reaction.

The performance of Cu-based activated carbon in NO reduction is related to their surface chemistry, namely the presence of nitrogen. N-groups significantly increases the activity of carbon materials.

Potassium and some transition metals, such as iron, copper, cobalt and nickel, have been used as catalysts in NO reduction. Although copper by itself has demonstrated good catalytic activity, its stability is limited. As such, bimetallic catalysts containing copper and potassium were developed. It was verified that the presence of potassium promotes a

better performance of the catalyst. The AC_M_BM@5Cu5K sample presented the best catalytic activity, obtaining complete conversion at 410 °C.

The stability of the most promising catalysts was evaluated. Fig 2. shows the NO conversion profile obtained during 100 h at 400 °C for the AC_M_BM@10Cu sample. This temperature was chosen to obtain a conversion of 90%.
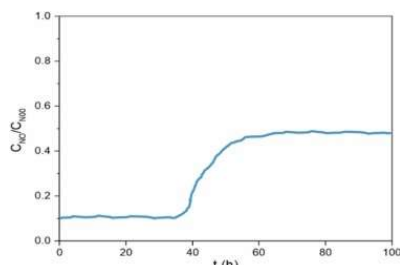

Fig. 2 Dimensionless concentration of NO on a stability test

The sample maintained a 90% conversion during 36 h of reaction. After this time, the sample began to lose activity, reaching a NO conversion of 52%, remaining constant after that.

For the AC_M_BM@5Cu5K, the stability test was also performed (not shown) and remained constant during 40 h of reaction, when it started to deactivate.

<u>NO reduction: structured catalysts</u>

Structured catalysts represent an attractive alternative to conventional powder catalysts as they offer better heat and mass transfer, reduced pressure drop and superior thermal and mechanical stability. Melamine foam (MF) is a type of ultrafine fiber foam and has the benefits of low apparent density, high density structure and flexibility, excellent mechanical properties and porous structure, even after high temperature carbonization. These structures, which are not catalytically active, serve as support to give rise to a structured catalyst prepared by coating an active catalytic phase.

The objective of this work, in collaboration with the International Iberian Nanotechnology Laboratory (INL), was the synthesis and characterization of structured carbon catalysts, through the coating of a melamine foam using precursor solutions of carbon xerogels doped with nitrogen (using melamine (M) or urea (U) as N-precursors) and impregnated with copper, catalytically active in NO reduction.

Fig. 3 shows that MF_10Cu achieves a very different conversion value while MF_M_10Cu and MF_U_10Cu exhibit similar profiles, and the maximum conversion is close to each other. The achievement of these results is due to the fact that doping carbon materials with nitrogen increases the density of electrons, which results in better catalytic activity. It is clear that MF_U_Cu stands out in the catalytic activity of reducing NO compared to MF_M_10Cu and MF_10Cu [2].
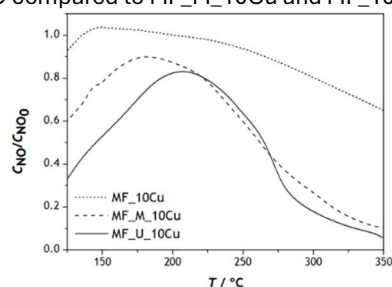

Fig 3. NO concentration in the presence of MF with [NO] = 1000 ppm in He with 5% of O_2.

The presence of transition metals in the structure was essential for catalytic activity, and the introduction of nitrogen groups in the catalysts resulted in enhanced catalytic results. The MF samples prepared with urea as N-precursor showed the best performance in reducing NO and simultaneously had the highest content of copper in their structure, so it appears that the incorporation/concentration of copper in the materials is a determining factor in the catalytic reduction of NO into N_2.

Future Work

NO reduction with carbon materials was extensively studied using different carbon material supports. However, it will be necessary to analyze the effect of the feed composition on NO reduction, carry out long-term tests to evaluate the stability of the catalysts under optimized conditions and try to elucidate the different stages of the mechanisms involved in NO reduction with and without oxygen.

By comparison, other carbon materials, such as carbon nanotubes (CNT) and carbon xerogels (XC), will be used as support for this reaction. CNTs represent an alternative to activated carbons for the following reasons: (i) high purity; (ii) excellent mechanical properties, (iii) high conductivity, (iv) high thermal stability and (v) absence of micropores, minimizing limitations to mass transfer. In the case of XC, its porous texture and surface chemistry can be adapted to the specific needs of the process. The application of these processes in industry requires the use of structured catalysts. In this context, the preparation, characterization and use of carbon monoliths would be of great interest.

Related Sustainable Development Goals

Outputs

Master Dissertations

Arnaldo Filipe Neto, Development of N-doped carbon catalysts for simultaneous NO reduction and CO, MIEQ, FEUP, 2020.
Mariana B. S. Felgueiras, Desenvolvimento de catalisadores de carbono para redução de NO, MIEQ, FEUP, 2021

Selected Publications

[1] P.S.F.Ramalho et al., Catalysis Today 418, 114044 (2023)
[2] Mariana B. S. Felgueiras et al., Catalysts 12, 170 (2022)

Team

Manuel F. R. Pereira, Professor/ Group Leader/ Full professor; **José L. Figueiredo** Emeritus Professor; **Olívia S. G. P. Soares**, Assistant Researcher; **Mariana B. S. Felgueiras,** PhD Student; **Patrícia S.F.Ramalho,** PhD Student.