Novel Ammonia Storage Materials for SCR Systems

Carbon Materials – Salt Composites

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Abstract

The emissions of nitrogen oxides (NO$_x$) are a serious environmental problem due to its relationship with the formation of smog, acid rain and because they are dangerous for human and animal health. These gases are produced in high quantities in diesel engines used for automotive applications, and different strategies are being used to reduce them, among which are the Selective Catalytic Reduction (SCR) systems. For its operation, it is necessary a supply of ammonia as NO$_x$ reducing agent, but the inefficiency at low temperatures of the systems used nowadays has led to the conception of the solid ammonia storage units (ASS). Unfortunately, the materials currently used, i.e. metal halides, do not meet the ammonia supply requirements at low temperatures and have problems of swelling and agglomeration.

In order to find a material with better properties for its application as an ammonia sorbent material, MgCl$_2$ composites with different carbon materials (graphite, graphene, and SWCNTs) were prepared by direct mixing and wet impregnation methods, and characterized in this work. Despite the decrease of total storage capacity, improvements were found in thermal stability and mass retention, as well as in sorption and desorption kinetics, making these materials a first result towards the improvement of the solid ammonia storage units.
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Chapter 1

Introduction

Nowadays, important interests are concentrated on improving and developing new technologies that can do front to global climate change and environmental problems. Humanity is facing a difficult horizon due to the increasing demand for traditional fossil fuels, the growth of undesirable and non-ecofriendly industrial practices and the multiple problems with modern transportation that remains to produce harmful emissions. The crescent desire of finding final solutions to all these problems is an issue of interest for several research centers and governmental organisms.

One of the most important involved sectors is the automotive industry, which plays a major role especially for its influence on global climate, human health, and energy sustainability. In this way, there are outstanding initiatives focused on research and development of cleaner combustion systems, as well as alternatives such as fuel cell application to mobility and electric cars \cite{5, 6}. A significant part of these efforts is centered on the reduction of harmful gas emissions and particulate materials, for that reason, different governments are following international agreements for facing these environmental problems and promoting research on the field. In the European context, the “Euro 6/VI vehicle emissions standards” set a guideline for the production of light- and heavy-duty vehicles with technical specifications for reducing the environmental impact. Specifically, these regulations include more stringent NO\(_x\) limits for diesel cars, as well as a new particulate material limit for gasoline direct injection engines. With a limit of 0.08 g of NO\(_x\) per kilometer, the Euro 6 standards decrease in an 84% the target for Light-Duty diesel vehicles in comparison with the Euro 3 level \cite{7}. These gases have a relevant contribution to smog production, acid deposition, acid rain, and eutrophication, which are also a cause of soil degradation and low water quality \cite{8}. Due to the importance of following these standards, particularly the case of emissions, this project will be focused on an approach to decrease nitrogen oxides production in diesel vehicles.

In order to achieve the Euro 6/VI standards, the automobile industry has to deal with advances in the full suite of the vehicle engine and the after-treatment design for reducing nitrogen oxides emissions \cite{7}. Different approaches will be discussed in more detail, but the main interest during this work will be the use of Selective Catalytic Reduction (SCR) as an exhaust after-treatment technology that involves the injection of a reducing agent, which is stored in a separate tank, to chemically break down the NO\(_x\) \cite{9}. The central problem for improving SCR application is leading with the storage of the reducing agent, therefore, some efforts are on the
design of new NH$_3$-SCR technology. As we will see, NH$_3$ as a reducing agent for SCR is stored in an Ammonia Sorbent System (ASS) unit, the interest of the present project is centered on improving its performance at vehicle operating conditions.

The main constituent of the storage unit is the sorbent material, NH$_3$ can be stored in a variety of materials under different pressure and temperature conditions, but it is the effect of sorption mechanisms that are key to awaiting better kinetics and storage capacities. Different materials are being investigated due to their properties for ammonia storage, mainly compounds that can store it via chemical sorption (absorption), but the faster and easier kinetics of physical sorbents are taking important interests on research. For these reasons, the main idea of this project is to formulate and test new composite materials based on the idea of mixing the physical and chemical sorption mechanisms, for this purpose different mixtures of carbon materials with chloride salts will be investigated.

1.1 Objectives

In the first phase of the project, the aim is to establish the state-of-the-art regarding the different areas of knowledge involved in the present work. For that, a literature review will be performed on the general context of NO$_x$ emissions reduction technologies. Then, the SCR and ammonia sorption systems will be studied with closer interest, and finally, a detailed review on the materials used as ammonia sorbents will be carried out. As different problems in the current ammonia storage materials have been identified, the present project seeks to propose new composite materials that have more performing sorption kinetics, as well as better and more stable thermal behavior than traditional chloride compounds. For this, composites of carbon materials and magnesium chloride will be prepared, characterized and tested in laboratory ammonia sorption conditions. In the last stage of the work, a comparison between the proposed composites and raw magnesium chloride will be done looking at the different properties and characteristics of interest for the application.

1.2 Challenges and expected contributions

As it will be discussed later on, increasing the ammonia storage capacity of chloride salts is a difficult objective to achieve, then it is more interesting to concentrate efforts on ameliorating its sorption kinetics and thermal stability. Adding carbon materials with well known physical sorbent characteristics could be an interesting option, and the challenge of this project is to test its effect on the properties of magnesium chloride. Even if chloride compounds are currently used as ammonia storage materials, it is expected as a final result of this work, to find a composite material that presents better performance for this application, a difficult task having in consideration that all the interesting characteristics are codependent of each other, i.e. sorption capacity and kinetics, surface area, sorption mechanisms and thermal stability.
Chapter 2

Background

This chapter seeks to contextualize the aim and motivation of the project as well as giving more information about the theory related to the envisaged application and the research topic. In the same way, it is a review on the state-of-the-art, willing to settle a general framework to facilitate the understanding of the following sections of the document.

2.1 Nitrogen Oxides Emissions

The growth of the world population has led to an increase in the demand for fossil fuels in an unexpected way, the multiple uses of these resources are the main reason of our dependence, and each day, it is more clear that the reserves are limited [10]. Even if important economic aspects are involved in the consumption of fossil fuels, its widespread use is responsible for long-term environmental problems related to global warming and climate change, this is the reason of being a high priority concern for the world of today [11]. The main way of exploiting these resources is through the well-known process of combustion, one of the most important energy production processes and the most common working principle of vehicles in the world. Unfortunately, the high impact consequences of combustion are being reflected on the air quality, human and animal health, and ecosystems degradation, leading to a severe and important environmental impact that is directly translated in damage of the vegetation and fauna, the poor quality of water and soil, and finally, to the services they support [12].

Different compounds are produced during the combustion process, all of them are of concern due to their interaction with the environment, but some specific products are more harmful than others. Carbon dioxide (CO$_2$) and water (H$_2$O) are the primary combustion products, and they affect the environment through greenhouse effects and potential localized fog. The secondary products are compounds like carbon monoxide (CO), unburned hydrocarbons (HC), soot, nitrogen oxides (NO$_x$), sulfur oxides (SO$_x$), and oxides of metals, and they are considered as major pollutants that can cause health problems in humans and animals and can contribute to acid rain [13]. Nowadays, research is focused in reducing all these emissions by manipulating different parameters of the combustion systems, in this project, the envisaged application seeks to reduce the production of nitrogen oxides, one of the most dangerous combustion products.
NO$_x$ is a generic term that refers to nitrogen oxides, some combinations of gaseous nitrogen and oxygen, typically NO and NO$_2$, which form at high combustion temperatures [14]. Nitrogen and oxygen react due to the high peak combustion temperature and availability of oxygen during the combustion, which are the main reasons for the formation of NO$_x$ [15]. The interest in reducing nitrogen oxides is because it is the main cause of smog and acid rain. Smog is cause breathing problems and allergies, and acid rain has especially harmful effects on plants, aquatic animals, and buildings. The subsequent impacts are significant, including adverse effects on ecosystems, the decrease of biodiversity, changes in species composition and dominance, and toxicity effects [16].

Nitrogen oxides are produced by different sectors as transports, energy production industry, agriculture, and manufacturing industries, but the main way is through fuel combustion, for example in power stations, cars, boilers, and stoves [14]. One of the sectors with the greatest influence on the consumption of petroleum derivatives is the automotive and transportation industry, as a consequence of that, the share of NO$_x$ production by this way is especially high. Only in Sweden, emissions of NO$_x$ amounted to 131,5 kt in 2015, and the largest source by 2016 was the transport sector, where emissions came to be 52,9 kt, corresponding to 40% of total emissions [17].

In general, NO$_x$ emissions have been reduced in the transport sector by 66% since 1990, and specifically for passenger cars, the reduction was of 68% during the period of 1990 to 2016 [17]. Stricter emission requirements for passenger and cargo vehicles are the main reason for this enhancement, in fact, during that time many governments have introduced laws to reduce these emissions [13, 18]. However, in the very last years, the reduction of nitrogen oxides emissions have been affected by the increasing demand of diesel vehicles due to its low CO$_2$-emissions, as well as a tangible difference between the Euro VI/6 standards and the real driving emissions (RDE) in this kind of cars [17, 19]. As is known, diesel engines offer the possibility of combining very high thermal efficiencies and good fuel proficiency, which results in low carbon dioxide emissions. The main problems for diesel engines are the emissions of nitrogen oxides NO$_x$ and particulate material. Diesel engines operate at a higher temperature and pressure than petrol engines, these conditions favor the production of nitrogen oxides and it depends on multiple engine design factors [15, 20]. Diesel engines are not only used for passenger cars, but they also have a considerable share in transportation and construction machines for the sake of their high fuel efficiency and durability [21].

Improving the operation of diesel engines for use in cargo and passengers vehicles is a challenge that the automotive industry is facing today. The reduction of emissions of gases such as nitrogen oxides is of main importance to make the use of these type of engines less harmful to the environment and human health. A variety of approaches have been proposed during the last years for achieving a higher efficiency in diesel engines, but at the same time reducing the production of harmful gases, especially NO$_x$. In the next section of this chapter, the different methods to reduce the content of nitrogen oxides on the exhaust gases in diesel engines will be reviewed and explained.
2.2 Diesel Exhaust Treatments

Regarding the Euro 6/VI standards, the automobile industry has to deal with advances in the full suite of the vehicle engine and the after-treatment design for reducing nitrogen oxides emissions [7]. NO\textsubscript{x} emission control systems have been provided by several vehicle manufacturers since 1970 [15], but the high standards of the actual legislation cannot be achieved solely by improving engines and combustion systems, rather some sort of after treatment must be used [22]. In the case of diesel cars, there are three main possibilities for accomplishing the emissions target. The first one is called In-cylinder Control (ICC), which is a combination of different strategies such as Exhaust Gas Recirculation (EGR), compression ratio reduction, use of two-stage turbocharging, variable valve lift, combustion chamber reshaping, and a reduction of fuel injection pressure [8]. The second option is known as Lean NO\textsubscript{x} Traps (LNTs), a system of oxidation and reduction catalysts with a NO\textsubscript{x} adsorber that stores the gas for successive reduction to N\textsubscript{2} and O\textsubscript{2}. And the last strategy, Selective Catalytic Reduction (SCR) that is an exhaust after-treatment technology that involves the injection of a reducing agent, which is stored in a separate tank, to chemically break down the NO\textsubscript{x} gases via a catalytic system [9].

The main objective for NO\textsubscript{x} control in diesel vehicles is to combine these different methods to get a solution for future emission regulations [20] [23], but it still multiple problems in each strategy that has to be fixed in the shortest possible time [24]. In the present work, the interest is centered in the SCR strategy as an after-treatment emissions control package, this technology was introduced on power plant applications in Japan more than four decades ago, and about twenty years later it was adopted for use in heavy-duty diesel vehicles [25]. Even after all this time of use as a deNO\textsubscript{x} process, SCR still has some important limitations unsolved, and fixing these problems is the key for achieving better performance and lower nitrogen oxide emissions in vehicles. In the next section, SCR technology will be discussed in more detail as well as the working principle and restrictions.

2.3 SCR technology for nitrogen oxides reduction

As said, Selective Catalytic Reduction (SCR) has been applied to stationary source fossil fuel-fired combustion units for emission control since the early 1970s [26], but the automotive application appeared in more recent years. At present, this technology has been specially improved for high-duty vehicles, but its use in lighter vehicles has presented some complications because of the low exhaust temperature, some big vehicle companies are developing its use for passenger vehicles as well [1]. The most common variation of SCR technology is the urea-SCR process. Due to ammonia’s toxicity, it is more common the use of an eutectic 32.5 wt% urea-water solution (UWS), also known as AdBlue or diesel exhaust fluid, as a carrier fluid that is injected into the hot exhaust upstream before its arrival to the catalytic reactor, this kind of NH\textsubscript{3}-SCR technology has a long application in the automobile industry [2] [27]. As it is possible to see in Fig 2.1, the traditional urea-SCR system consists of a diesel engine, a urea injecting system, and the SCR catalyst reactor; but more modern systems could have other optional constituents depending on the design of the vehicle as a Diesel Oxidation Catalyst (DOC), a Diesel Particulate Filter (DPF) or an Ammonia Slip Catalyst (ASC) [23].
After the urea is sprayed into the hot exhaust gas stream, ammonia is formed in the initial part of the SCR catalyst by the heating effect of the exhaust gas, and then it reacts with NO\textsubscript{x} completely to form N\textsubscript{2} and H\textsubscript{2}O \cite{2, 28}. The main reactions of the system take place in the SCR unit, and they are known as reduction reactions of NO\textsubscript{x} compounds, but also it is possible to find the release reactions of ammonia from urea. All these reactions are listed below, equations 2.1 and 2.2 are the formation of NH\textsubscript{3} and 2.3 to 2.6 are the reduction of nitrogen oxides, in this process is really important the control of temperature in the catalytic reactor, high temperatures could cause oxidation of ammonia, and with this, a decrease of the general performance of the unit \cite{29, 30}.

\begin{align*}
\text{H}_4\text{N}_2\text{CO} &\rightarrow \text{NH}_3 + \text{HNCO} \quad (2.1) \\
\text{HNCO} + \text{H}_2\text{O} &\rightarrow \text{NH}_3 + \text{CO}_2 \quad (2.2) \\
4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 &\rightarrow \text{N}_2 + 6 \text{H}_2\text{O} \quad (2.3) \\
2 \text{NH}_3 + \text{NO} + \text{NO}_2 &\rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} \quad (2.4) \\
4 \text{NH}_3 + 6 \text{NO} &\rightarrow 5 \text{N}_2 + 6 \text{H}_2\text{O} \quad (2.5) \\
8 \text{NH}_3 + 6 \text{NO}_2 &\rightarrow 7 \text{N}_2 + 12 \text{H}_2\text{O} \quad (2.6)
\end{align*}

The use of urea as ammonia carrier is an advantage regarding easy handling and safety, this liquid commercially known as AdBlue is normally stored as a solution in a tank, which has to be refilled every so often. But the advantages are not enough when it is compared with all the practical problems. In the real application, UWS droplets are deposited on the system components due to the incomplete evaporation and thermal decomposition of urea, leading to a reduction of the NO\textsubscript{x} conversion efficiency \cite{31}. The high cost of the system, CO\textsubscript{2} production, urea crystallization, coking, and low effective ammonia content are disadvantages that have led to think of other types of technologies for reducing nitrogen oxides emissions as well \cite{2, 32}. For these reasons, the central problem for improving SCR application is leading with the ammonia storage system and therefore, some efforts are in the design of a new NH\textsubscript{3}-SCR technology.
As discussed before, ammonia handling and transport are difficult and because of this, it is desired to avoid any safety problem; in this way, one of the most suitable designs consists in an ammonia storage system that works with a solid material as NH$_3$ source [2, 32]. This system is safer and more stable, and also profits of the energy in exhaust flow, increasing the general efficiency of the diesel vehicle. In Fig 2.2 it is possible to appreciate the changes in comparison with the traditional urea-SCR system. The main difference is the addition of an Ammonia Sorbent System (ASS) that is now installed in the position where the urea tank (AdBlue) was before and nearby the exhaust pipe, making the utilization of heat more appropriate [2].

Figure 2.2: Diagram of a sorbent-SCR system with an ASS unit [2].

Comparing with the traditional urea-SCR system, an ammonia-based SCR technology solves one of the most significant problems in the catalytic reactor: conversion of urea to ammonia does not take place completely below 200°C (Eq 2.1-2.2), especially the isocyanic acid hydrolysis step [33]. Then, the availability of gaseous ammonia makes possible to obtain NO$_x$ conversion throughout a greater exhaust temperature range, including low temperatures as during urban driving conditions [3]. In general, all the parts in the sorbent-SCR system are being investigated and upgraded, but the interest of the present project is centered on improving the performance of the ASS unit through amelioration of its main constituent: the sorbent material. In the next section, the ASS unit will be explained in more detail, as well as its working principles.

2.4 Ammonia Sorbent System and working principles

The development of ASS technology for SCR has been carried out during recent years, the Danish start-up Amminex is one of the companies involved, now part of the French group Faurecia, that developed a system of storage and diffusion of ammonia for reduction of NO$_x$ emissions in diesel engines called ASDSTM [34]. These Ammonia Sorbent Systems are composed of two replaceable main cartridges and one small, permanently installed start-up unit. In Fig 2.3 the smaller start-up unit is activated after starting the engine and the main cartridge are available during the first 4-8 minutes of operation, depending on the size and design of the unit. Then, when the main tank achieved the appropriate pressure, the ammonia supply is changed from the start-up unit to dose from the main unit. When the
auxiliary unit is not working, it cools down and reabsorbs NH$_3$, with this strategy it is ammonia available each time the engine is started [3].

Typically, an ASS unit is filled with an ammonia storage material that can release this compound in gas form when the temperature increase. As the operating principle of the ASS is the sorption process, it has to be preheated by an electric heater before the vehicle is started, and after it will be switched to heating thought exhaust gas [2]. The main constituent of the storage unit is the sorbent material, NH$_3$ can be stored in a variety of materials under different pressure and temperature conditions, but it is the effect of sorption mechanisms that are key to awaiting better storage capacities.

After the nature of the species involved in the sorption process, pressure and temperature are the most important variables. In the case of the ASS unit, the ammonia is desorbed when the pressure in the unit is higher than the equilibrium reaction pressure, for that the solid sorbent is heated along D–A in Fig 2.4. The desorption happens at point A, then the ammonia gas is injected to the exhaust gas pipe for subsequent reaction in the SCR unit, represented by the line A-B (theoretical equilibrium) or A-B’ (real desorption process). When all the stored ammonia in ASS unit has been used, it is necessary to refill it using a sorption/storage process.
In this procedure, the ASS unit is connected with an ammonia tank and cooled by an external cooling method for decreasing temperature and pressure inside the unit, it is the line from point A to point D. The ammonia tank is kept at least 5°C higher than the sorption temperature inside the ASS unit to avoid the condensation to happen inside the ASS unit; ammonia is stored until it reaches saturation, represented by the line D-C [2, 4, 32].

The term sorption is a reference to the joint effect of adsorption and absorption. The adhesion of atoms, ions or molecules of gas, liquid or dissolved solids to a surface is called "adsorption". In the adsorption process, two substances are involved: the first one, the solid or liquid on which adsorption occurs and it is called "adsorbent"; the second one, is the "adsorbate", which is the gas or liquid or solute of a solution that adsorbs on the surface. Adsorption is different from absorption, in the second one, the molecules of a substance are uniformly distributed in the mass of another, while in adsorption the molecules of the substance are present in a higher concentration on the surface of the other [35]. Depending on the type of material, the storage system is based either on physical sorption (physisorption) as in the case of porous materials, or on chemical sorption (chemisorption) as in the case of metal halides. Physisorption is the mechanism by which gases are stored in the molecular form, i.e. without dissociation, on the surface of a solid material. The weak dispersive forces, called van der Waals forces, between the gas molecules and the atoms on the surface of the solid, are responsible for the molecular adsorption. If the attractive force between the adsorbate and the adsorbent is almost as strong as the chemical bonds, the adsorption is called chemisorption or chemical sorption. Physisorption is a completely reversible process, which means that gases can be easily adsorbed and released for several cycles without any loss; in chemisorption, the attractive force is very strong, so the reverse process cannot be easily achieved [36, 37].

In order to store ammonia with high efficiency at moderate conditions, many efforts are in the research of new methods for storing ammonia in solid-state materials [38]. Depending on the sorption mechanism, ammonia storage materials can be classified into two main groups: chemical or physical sorbents. In general, chemical sorbents are compounds that can form ammine complexes with a chemisorption reaction, especially all kinds of inorganic halides are well known for this application, and they flexibly adjust to external conditions; this reason makes them an alternative which has been widely applied in various fields such as refrigeration, heat pump, energy storage, and electricity generation [32, 39]. In the same way, ammonia has been recognized as a promising hydrogen carrier due to its several desirable characteristics, this potential use of NH₃ impulse research of a large number of ammine complexes that can be used as sorbent material in the ASS unit. On the other hand, physical sorbents are mainly porous materials that possess high specific surfaces as carbon materials, porous polymers, zeolites, and other ceramics [40]; therefore, its application to ammonia storage as a single material is no widely studied, but it is a research trend as composites with inorganic salts [41].

Having in mind how works the sorbent-SCR process and the ASS unit, it is necessary to do a general review of the sorbent materials that can be used for this purpose. In the next section, it is possible to find an overview of the state-of-the-art on ammonia sorbent materials.
### 2.5 State-of-the-art on ammonia sorbent materials

As discussed before, solid ammonia storage is an interesting method to reduce the risk due to difficult handling liquid ammonia at high pressure, as well as a way to achieve a high degree of safety regarding the possible failure of the tank. In the same way, it is important to use materials that allow high volumetric storage capacity with low-cost production [3]. For this purpose, different kind of materials have been explored and tested, and some chemical sorbents are being used in the present for SCR applications. Between them, inorganic halides are the most studied group of compounds and they form stoichiometric ammine complexes, the general reaction can be written as follows [39]:

\[
\text{halide} \cdot m\text{NH}_3(s) + (n-m)\text{NH}_3(g) \rightleftharpoons \text{halide} \cdot n\text{NH}_3(s)
\] (2.7)

This reaction is only one step, but in reality, multiple steps can be part of the chemisorption reaction. The equilibrium for these reactions shows a linear relation in \(1/T\) vs. \(\ln P\) plots, as in Fig 2.4, and can be described by the Clausius–Clapeyron equation as in Eq 2.8. \(\Delta H\) and \(\Delta S\) represent the enthalpy and entropy changes for the reaction. If the complete reaction presents multiple steps, it is possible to apply this relation to every single step [39].

\[
\ln(P_{\text{NH}_3}) = -\frac{\Delta H_r}{RT} + \frac{\Delta S_r}{R}
\] (2.8)

Metal borohydrides are one of the options for ammonia storage, thermodynamic properties of ammine complex of these compounds have been reported as hydrogen storage materials, but there are not a lot of studies reporting their properties for this application. Nevertheless, one systematic research about ammonia absorption on metal borohydrides has been developed [42]. The general chemisorption reaction for these compounds is presented in Eq 2.9.

\[
\text{M(BH}_4\text{)}_{m(s)} + n\text{NH}_3(g) \rightleftharpoons \text{M(NH}_3\text{)}_n\text{(BH}_4\text{)}_m
\] (2.9)

Some of the studied compounds were Mg(BH\(_4\))\(_2\), Ca(BH\(_4\))\(_2\), LiBH\(_4\), NaBH\(_4\) and KBH\(_4\), among which stands out NaBH\(_4\), that has moderate properties as NH\(_3\) storage materials because the operation PT are close to ambient conditions (96 kPa, 293 K) [38]. Another option for storage material is the group of the metal halides, several studies support that these compounds can absorb a large amount of ammonia to generate ammine complexes and their volumetric densities are comparable with liquid ammonia [38]. Eq 2.10 shows the reaction between the metal halide and ammonia to form the ammine complex, where M is a metal and X is a halogen [42].

\[
\text{M(X)}_{m(s)} + n\text{NH}_3(g) \rightleftharpoons \text{M(NH}_3\text{)}_n\text{(X)}_m
\] (2.10)
Even if different metal halides have been investigated, only some of them are profitable for ammonia storage systems, the main reasons are the complex structural changes during the formation of the ammine complex and instability in the presence of CO\(_2\) or H\(_2\)O (i.e. LiF, LiBr, NaI, and others). Especially, metal chlorides and bromides have been studied for ammonia storage units, but considering the temperature range of the exhaust gas and the tolerance limit of vehicle materials, the operation conditions of the sorbent-SCR system restricts the variety of sorbent materials to middle-temperature salts (MTS) and low-temperature salts (LTS), i.e. salts with desorption temperature no more than 150°C with respect to the condensation temperature of ammonia [32]. Metal chlorides are a good option regarding the operation temperature, some studies of different compounds such as CaCl\(_2\), SrCl\(_2\), NiCl\(_2\), MgCl\(_2\), MnCl\(_2\), and BaCl\(_2\) said that they could be suitable for ammonia storage only having in mind their chemical equilibrium. In this way, important results of storage capacity and sorption kinetics of MnCl\(_2\) and NiCl\(_2\) have been reported, doing of these compounds interesting options [43]. One of the most important chloride salts for ammonia solid storage is SrCl\(_2\) because of its experimental sorption capacity and unit price [32].

Nowadays, strontium chloride is one of the best examples of application to ammonia storage. The commercially known material AdAmmine\textsuperscript{TM} developed by Amminex Emissions Technology can hold large quantities of ammonia (approx. 450g of NH\(_3\) per solid liter) and release its content gradually if heated. Compared to the operating costs of conventional liquid-based NO\(_x\) reduction, AdAmmine\textsuperscript{TM} is cheaper and safer; also improvements in installation, handling, and reuse are part of the main characteristics of the product [44]. Similarly, MgCl\(_2\) has been applied to SCR systems, ammonia can be stored safely in metal ammine complexes with the formula Mg(NH\(_3\))\(_n\)Cl\(_2\) with \(n = 6, 2, 1\), in which all ammonia desorption occurs at temperatures between 410-700 K [45]. In fact, the magnesium chloride complex with \(n = 6\) is quite advantageous regarding ammonia density, a single-crystalline compound of Mg(NH\(_3\))\(_6\)Cl\(_2\) has an ammonia density of 38 kmol NH\(_3\)/m\(^3\), whereas that of liquid ammonia is 40 kmol NH\(_3\)/m\(^3\) [46]. The saturated complex is obtained in three absorption steps [3, 46]:

\[
\begin{align*}
\text{MgCl}_2(s) + \text{NH}_3(g) & \rightleftharpoons \text{Mg(NH}_3\text{)Cl}_2(s) \\
\Delta H_r &= -87.0 \text{ kJ/mol NH}_3, \; \Delta S_r = 230.88 \text{ J/K.mol NH}_3 \\
\text{Mg(NH}_3\text{)Cl}_2(s) + \text{NH}_3(g) & \rightleftharpoons \text{Mg(NH}_3\text{)}_2\text{Cl}_2(s) \\
\Delta H_r &= -74.9 \text{ kJ/mol NH}_3, \; \Delta S_r = 230.30 \text{ J/K.mol NH}_3 \\
\text{Mg(NH}_3\text{)}_2\text{Cl}_2(s) + 4 \text{NH}_3(g) & \rightleftharpoons \text{Mg(NH}_3\text{)}_6\text{Cl}_2(s) \\
\Delta H_r &= -55.6 \text{ kJ/mol NH}_3, \; \Delta S_r = 230.63 \text{ J/K.mol NH}_3
\end{align*}
\]

In these reactions, the desorption direction is endothermic, i.e. requires some energy to start the process, and the equilibrium could be modeled with the relation of the Eq 2.8. From that, it is possible to know that the vapor pressure of Mg(NH\(_3\))\(_6\)Cl\(_2\) is about 2.2 mbar at room temperature, being 30000 times less volatile than liquid ammonia [3]; one of the most important features of this compound regarding safety.
and handling. In the same way, full ammonia-sorbed magnesium chloride presents a high mass density of 1252 kg/m$^3$, compared with approx. 1090 kg/m$^3$ of AdBlue at 20°C [47], that allows the same use of ammonia with much less storage volume [3]. In other applications, magnesium chloride has been reported as promising candidate for thermochemical storage based on its volumetric energy density [18]. Knowing this, it is possible to say that a system based on solid ammonia storage can offer safety, low storage volume, high ammonia storage capacity, and during operation, only pure ammonia gas is released decreasing the risk of blockages in the SCR system [3]. The disadvantages of an ASS unit based in chloride salts are, according with some studies after several thermic cycles, the relatively low thermal conductivity of this kind of chemical sorbents and the swelling/agglomeration that will lead to low heat and mass transfer performance [49, 50]. In the case of MgCl$_2$, the change of density between the initial state (2325 kg/m$^3$) and the full filled complex (1252 kg/m$^3$) leads to an expansion of approx. 3.85 times the initial molar volume [46], a problem for the design of the storage unit.

For these reasons, different proposals of composite sorbents of chloride salts-porous media for ammonia storage are now a research trend. A variety of porous media as expanded graphite, carbon fibers, activated carbon, silica gel, vermiculite, zeolite, and other ceramics, have been studied for enhancing heat and mass transfer performance and increasing the sorption quantity at the same time. Also, porous metal oxides, clay mineral, resins, and synthesized polymers have been proposed [2, 51, 52]. Studies in thermochemical heat storage remark that the chemical composition and pore structure of porous materials affect the sorption capacities of their composites [53], affirmation also valid for other applications of their sorption properties. Following, it will be listed some of the chloride salt/porous media composites used as sorbent material in recent studies.

A first example is the use of mesoporous materials as supports, in this case, silica gel, alumina and bentonite were used for CaCl$_2$-containing composites for water sorption; it was found that the addition of porous structures enhances in each case the sorption capacity [53]. Another case is the use of ion-exchanged Y-zeolites (Co-Y, Cu-Y, and Na-Y) but without significant results for big scale applications [52]. A big group of porous materials with extensive use for improving chloride salts properties is formed by various carbon materials. Between them, one of the most used is the Expanded Natural Graphite, for example, in SrCl$_2$ impregnated with ENG and carbon coated aluminum, it was demonstrated that thermal diffusivity and mass transfer performance were improved as well as a reduction of the desorption time [49, 50]. In the same way, multi-walled carbon nanotubes were used as the porous matrix for a CaCl$_2$ composite due to its macroporous structure and large specific surface areas, even if the final material has a small improvement in the sorption capacity of ammonia, prevention of agglomeration and attenuation of the sorption performance have been the remarkable results [54]. Sorbent composites are used in other applications, refrigeration is one of them, and the use of CaCl$_2$-activated carbon materials to improve the mass and heat transfer performances has been demonstrated [55].

After this literature review, it is possible to have a general idea about the performance of the sorbent-SCR system, its ASS unit and the principles of working of
this method for NO$_x$ emissions reduction. Knowing the existence of the different issues to improve on the ammonia storage system, this project wants to propose a new composite sorbent for the ASS unit based in chloride salts and two different carbon materials. In that way, MgCl$_2$ will be used as sorbent salt due to its well-known properties and extended use as ammonia storage materials, composites with graphite, graphene and single-walled carbon nanotubes (SWCNTs) will be manufactured. The selection of these carbon materials obeys to its porosity, thermal properties and its relatively low cost in comparison with other C-based materials. If appropriate results are achieved, composites with other salts, i.e. SrCl$_2$ or CaCl$_2$, can be considered in the future. The interest of this research is to produce a composite with better properties than other sorbent materials in the market but also with opportunities for economic competence. The strategy that will be proposed for achieving these objectives involves two different mixing methods of the chloride salt with the carbon materials, and it is possible to find more information, as well as the characterization techniques that will be used, in the next section.
Chapter 3

Methodology and Experimental Description

3.1 Materials and equipments

The following compounds were employed for this work: Magnesium Chloride (MgCl₂, anhydrous, 99%, Alfa Aesar), Single-Walled Carbon Nanotubes (carbon ≥85, >70 as SWNT, diam. 1.3-2.3 nm, Aldrich Chemistry), Graphene Nanoplatelets Aggregates (sub-micronparticles, S.A. 500 m²/g, Alfa Aesar) and Graphite (99% in powder, APS 7-11 μm, Alfa Aesar). SWCNTs were pretreated to eliminate soluble impurities by immersion and stirring in ethanol (99.9 % purity) during 3h, filtering with vacuum pump and drying at 125°C during 3h.

The BET (Brunauer–Emmett–Teller) surface area of the samples was measured with a Gemini VII 2390 Surface Area Analyzer (Micro- meritics, Norcross, USA) by N₂ adsorption at 77.3K (liquid nitrogen temperature). Scanning electron images were obtained with a SEM JSM-IT300LV (JEOL GmbH, Germany) to characterize the microstructure of the composites. For studying the thermogravimetric behavior of the samples and the ammonia sorption process, it was occupied a Simultaneous Thermal Analyzer DSC/TGA (SDT 650, TA instruments, USA).

3.2 Direct Mixing

A conventional mechanical mixing method was used to produce some of the composites: ball-milling of the salt with graphene and graphite during 2 h with a proportion of beads/material of 1:5. Different compositions have been made for studying the influence of the carbon materials on the properties of the salt. In Table 3.1, it is

<table>
<thead>
<tr>
<th>Composite name</th>
<th>CM content (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite+MgCl₂</td>
<td></td>
</tr>
<tr>
<td>Gt1</td>
<td>1</td>
</tr>
<tr>
<td>Gt10</td>
<td>10</td>
</tr>
<tr>
<td>Gt20</td>
<td>20</td>
</tr>
<tr>
<td>Graphene+MgCl₂</td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>1</td>
</tr>
<tr>
<td>G10</td>
<td>10</td>
</tr>
<tr>
<td>G20</td>
<td>20</td>
</tr>
</tbody>
</table>
possible to find the carbon material (CM) content, the remaining percentage corresponds to MgCl$_2$.

3.3 Wet Impregnation

Composites of pretreated SWCNTs with MgCl$_2$ were prepared via wet impregnation based on the method proposed by Grekoba et al. [56, 57] for the impregnation of MWCNTs with chloride salts. For this, saturated solutions of magnesium chloride with in water and water/ethanol (1:1 in volume) were prepared and stirred during 40 min at room conditions. Then, 0,1 g of SWCNTs were introduced in 20 mL of each solution, keeping the stirring during 1 h. After, the solutions were filtered with the help of a vacuum pump, this product was shaped into tablets of $\sim$8 mm and $\sim$4 mm (for salt retention and ammonia sorption tests, respectively) and, finally, the samples were dried at 125$^\circ$C during 3 h.

3.4 Salt retention tests

To check the thermal stability and salt retention of the composites after the melting point of MgCl$_2$, tablets of $\sim$8 mm of the direct mixed compounds have been used in this work. A Specac manual hydraulic press was employed to make tablets of around 50 mg with 3 ton of load. The thermal treatment cycle was the same in all cases: heating from RT to 800$^\circ$C using a heating/cooling rate of 5$^\circ$C/min and 30min at high temperature. A Nabertherm tubular furnace (RHTC 80-230/15) was destined for this purpose, with Ar flow for protecting the samples of oxidation.

3.5 Characterization techniques

3.5.1 SEM/EDS

SEM images at different magnifications were taken in all stages of the work with a JEOL JSM-IT300LV, starting with the raw materials for looking their main characteristics and morphology, when mixing and pressing special attention was on the distribution of the compounds in the tablet surface, and finally, after each thermal treatment in order to check if any change has occurred.

3.5.2 Surface area and adsorption measurements

With the Gemini VII 2390 Surface Area Analyzer, it was possible to analyze the surface area of the composites, samples with an approximate mass of 100 mg were studied in these experiments. Nitrogen was used as adsorbed gas and its relative pressure ($P/P_o$) was changed between 0.01 and 0.9 with 40 points in geometrical distribution for low pressures, a bath of liquid nitrogen ensures isothermal conditions at 77.3 K in all the experiences. Important information was collected from the isothermal adsorption curves and the BET surface area calculations have been done for $0.05 < P/P_o < 0.15$. Experiments have been repeated three times in all cases, and in these work it will be presented a value with standard deviation.

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3.5.3 TGA/DSC of raw materials in Ar

Thermal analysis of the samples under inert atmosphere was carried out for raw materials and composites. Argon flow (50 mL/min) was used during the experiences for protecting from oxidation and studying the release of water and gases, as well as finding the melting point of the MgCl$_2$. For this experiences, an increase in temperature from RT to 800°C with a heating rate of 10°C/min was used for looking for this basic information.

3.5.4 Ammonia sorption experiments

The very first part of the present work was focused on the definition on a sorption experience that gives the most accurate information about this process. For that, it was important to have into account the results of degassing step studied before and the parameters of the real application. Here it will be presented the procedure that was finally used, but later on it will be explained how it was appointed. Two different sorption programs have been used for studying the absorption of ammonia and the release under argon and ammonia atmospheres. Both of them start with a degassing step that follows the scheme shown on Fig 3.1, with an Ar flow of (50 mL/min). Then, ammonia absorption is the next step in both programs, a change of atmosphere from Ar to NH$_3$ (100 mL/min) and a temperature of 25°C were employed until saturation of the sample (∼30 min).

The desorption step is the main difference between both programs, the first one studies the behaviour under argon atmosphere (50 mL/min) with different changes.

---

**Figure 3.1:** Degassing of samples

**Figure 3.2:** Conditions setting for the ammonia sorption and desorption tests under argon atmosphere
on the temperature. On Fig 3.2 is possible to see the evolution of temperature during these experiences, its aim is to see the performance of the materials at two different isotherms (35 and 60°C) and the step at higher temperature (200°C) is to verify the total release capacity. On Fig 3.3 is possible to find the evolution of the experience parameters of the second type of experience. After the absorption, the ammonia atmosphere is maintained and the temperature is increased until 200°C, the idea is to understand the materials behaviour under real operative conditions. When stabilization is achieved, the atmosphere is changed to Ar (50 mL/min) to check the release capacity, in the same way that in the first experience.

![Figure 3.3: Conditions setting for the ammonia sorption and desorption tests under ammonia atmosphere](image)

Finally, in both cases the temperature of the furnace is cooled down with a flow of air. With this set of experiences, it is possible to find enough data about the performance of the different samples used for this work.
Chapter 4

Raw materials characterization

The present chapter will be focused on the characterization of raw materials, for this purpose, different experiences have been carried out as well as techniques that allow us to know about their morphology, size distribution, surface area, and thermogravimetric behavior. As said before, two different kinds of materials have been used in the present work. The main component of the composites is a metal halide, Magnesium Chloride (MgCl$_2$), well known as ammonia sorbent applied before in SCR technology. To enhance different properties of this salt as ammonia carrier, three carbon allotropes have been used based on their special characteristics that will be discussed during the following sections.

4.1 SEM images and morphology

SEM characterization was used to determine the morphology and micro-structure of the raw materials. In Fig 4.1, it is possible to find four SEM images, one of each raw material. In general, it is possible to appreciate a random distribution of sizes and uniformity in morphology. MgCl$_2$ is a salt in the form of crystals of different sizes and shapes that can not be easily described, it is not possible to determine a unique morphology, but the dimensions of the particles are in the range of about 500 $\mu$m to some tens of microns; in the case of Fig 4.1a, it has been especially difficult to take an appropriate image because of the non-conductive nature of the chloride salt, even using Pt coating the quality does not improve considerably. Fig 4.1b corresponds to graphite, it is possible to see the typical sheets conforming the morphology of this carbon allotrope with different thickness and sizes but with uniformity in a general way, it was possible to rectify the average particle size of approx. 10 $\mu$m. Graphene used on this work is in the form of Nanoplatelets Aggregates (GNA), which could be verified by SEM microscopy; in Fig 4.1c, particles of different sizes in the scale of 10 $\mu$m can be found, but images at higher magnification allow to find platelets of some microns conforming these bigger aggregates. Finally, Fig 4.1d corresponds to the SWCNTs, there were found elongated conical bodies that are entangled and interlaced in a random way, they have diameters in the scale of few microns; in the same way, other types of larger and planar morphologies are appreciated that agree with the purity expected for the material used.

Equally, EDS measurements have been made on MgCl$_2$, graphite, and graphene without any remarkable result. In the case of SWCNTs, it was possible to rectify the purity of the material and the results are presented in the Table 4.1.
Figure 4.1: SEM images of raw materials: MgCl$_2$ (a), graphite (b), graphene (c), and SWCNTs (d).

It is possible to find the electron image and spectra from the EDS measurement. Content of total carbon of about 82% was found, with impurities of oxygen, sulfur and iron were calculated from EDS. The C-content is closed to the value indicated by the manufacturer, and as it could be verified by SEM, the SWCNT allotrope is the main constituent of the material, the remaining carbon content corresponds to carbonaceous impurities that can be in the form of nanographite or, as in this case, amorphous carbon [58]. The other impurities that have been found are common on carbon nanotubes, especially the Fe content that comes directly from the catalyst residues after synthesis [59]. The impurities can be removed from the carbon nanotubes by different methods, but it is difficult to achieve a high degree of purity without causing damages to the SWCNTs morphology [60]. In this work, simple washing with ethanol (99.9% purity) was used as a treatment to eliminate soluble impurities, but it will not be presented any result as no considerable difference was achieved.

Table 4.1: EDS results of raw SWCNTs.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>σ (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>82.18</td>
<td>1.04</td>
</tr>
<tr>
<td>O</td>
<td>1.22</td>
<td>0.26</td>
</tr>
<tr>
<td>S</td>
<td>0.73</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe</td>
<td>15.87</td>
<td>1.02</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
The presence of impurities in the SWCNTs that will be used for making composites with MgCl$_2$ should not be a problem for the considered application, this carbon material will be used as a mechanical reinforcement and to increase the physisorption properties of the salt, and no reaction between the impurities and the sorbent salt is spectated.

4.2 TGA/DSC characterization under Ar flow

In this section of the report, it is possible to find the thermogravimetric analysis and differential scanning calorimetry of the raw materials. Thermograms from RT to 800-900$^\circ$C are presented to determine the influence of the temperature on the stability under an inert atmosphere (Ar flow). Magnesium chloride used in this work presents some important behaviors that should be discussed profoundly. Fig 4.2 shows the evolution of the mass of a MgCl$_2$ sample and heat flow when the temperature is increased from RT to 800$^\circ$C at 10$^\circ$C/min. Several fluctuations in the heat requirements are present in the DSC curve, but the most important one is the endothermic peak at $\sim$715$^\circ$C that corresponds to the melting point of magnesium chloride.

![Figure 4.2: TGA/DSC from RT to 800$^\circ$C of MgCl$_2$.](image)

In theory, a sample of this salt without any content of moisture should not present important variation in the mass before arriving at the melting point, but here it is possible to see several changes throughout the temperature increase. The reason is the content of an important quantity of moisture in the sample, that promotes the formation of hydrated complexes of MgCl$_2$. In fact, magnesium chloride has the capacity of storing water in the same way that happens with ammonia. H$_2$O sorption is a well-known phenomenon that has been studied several times for different applications, and the reactions and kinetics have been defined by different methods. MgCl$_2$, being a high hygroscopic compound, can absorb water to form a hexahydrate complex, but in our case, the interest is in the dehydration process. Some authors
have proposed the following set of reactions to describe the water desorption process [61]:

\[
\begin{align*}
\text{MgCl}_2 \cdot 6 \text{H}_2\text{O} & \rightarrow \text{MgCl}_2 \cdot 4 \text{H}_2\text{O} + 2 \text{H}_2\text{O} \quad (T=117^\circ\text{C}) \\
\text{MgCl}_2 \cdot 4 \text{H}_2\text{O} & \rightarrow \text{MgCl}_2 \cdot 2 \text{H}_2\text{O} + 2 \text{H}_2\text{O} \quad (T=185^\circ\text{C}) \\
\text{MgCl}_2 \cdot 2 \text{H}_2\text{O} & \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} \quad (T=242^\circ\text{C})
\end{align*}
\]

But defining these reactions is a complex task that depends on multiple variables, i.e. the step of Eq 4.3 can easily go to Eq 4.4 if the conditions are not appropriate under rigorous anhydrous atmosphere [61]. In the same way, if the heating continues, another reaction will take place as described in Eq 4.5. In general, more elaborate and specific intermediate reactions have been proposed [62], but for the purposes of this work, these five reactions are enough to understand the behavior of the MgCl\text{2} used here.

\[
\begin{align*}
\text{MgCl}_2 \cdot 2 \text{H}_2\text{O} & \rightarrow \text{MgOHCl} + \text{HCl} + \text{H}_2\text{O} \quad (T=180^\circ\text{C}) \\
\text{MgOHCl} & \rightarrow \text{MgO} + \text{HCl} \quad (T=415^\circ\text{C})
\end{align*}
\]

In Fig 4.2, it is possible to say that a mass loss of approximately 9-10% during the heating from RT to 400°C is due to the decomposition of the hydrated MgCl\text{2} complexes. Heat flow fluctuations in the range of 180-250°C in endo and exothermic directions let know that the conditions of the system make possible the coexistence of reactions 4.3 and 4.4. At 400°C, it is sure that species as HCl and H\text{2}O are completely gone from the sample, but when the temperature reaches 415°C, the last reaction starts to form MgO during a long range of temperature that almost overlaps with the loss of mass related to the evaporation of salt when the temperature attains the melting point.

Even if it is not possible to say with exactitude how much of the initial sample correspond to hydrated complexes, it serves to define what kind of treatment is necessary before carrying out the ammonia sorption experiences with the composites during this work. To simplify the ammonia sorption kinetics, it is desirable to have MgCl\text{2} as the main component of the composite; in case of having hydrated complexes in high quantities, secondary reactions between them and ammonia will take place making the process more complicated to understand. For this reason, it was decided to perform a degassing of the composites at 400°C, in order to ensure that only MgCl\text{2} and a small (almost negligible) content of MgOHCl will be present in the composites. The existence of the last compound should not be a problem for the ammonia storage because of the quantity, taking into account that the total mass loss at 400°C in form of HCl and H\text{2}O is ∼9%, the final content of MgOHCl in the sample cannot exceed a 2-3% in weight.

Now, in the same way as in the case of MgCl\text{2}, it is necessary to know what happens with the carbon materials when the temperature is increased. In Fig 4.3, it is plotted the TGA curves from RT to 900°C of all the carbon materials that will be used during this work; each material presents a different behavior, but it is all that
was expected. Graphite, being a carbon allotrope with low surface area, does not have enough space to store species from the environment and its mass evolution when the temperature increases are quite stable with less than 0.5% of weight change. In the case of SWCNTs and graphene, they present a higher surface area and, in effect, it is possible to trap more species from the surroundings. SWCNTs show a final weight change of less than 3% and it is possible to differentiate some changes in the form of the curve, showing the capacity to adsorb different gaseous species and to release them by the action of the heating. Graphene, in a similar way, adsorbs gaseous compounds in more quantity and liberates them to have a final weight loss of less than 7%. As well, these materials can also liberate impurities that are present from their synthesis or contamination from other sources. At 400°C, the chosen temperature of pretreatment for the composites of this work, complete degassing is not possible for SWCNTs and graphene, but it is not a problem due to the low mass change in both of them.

4.3 Surface area measurements

One of the properties that are wanted to be improved is the specific surface area, this is a physical property of any material that is intimately linked to its particle size, porosity and other characteristics related to the microstructure. Normally, the surface area is determined by volumetric gas adsorption, that allows quantifying the surface of a material by evaluating the adsorption of a specific gas under different partial pressures [63]. Different models can be used to calculate the specific surface area of a material, but the BET model (Brunauer, Emmett, and Teller), based on the adsorption of a monomolecular layer of nitrogen on the surface of the sample, will be used to characterize the raw materials and composites during this work.

The Fig 4.4 shows the values of the BET surface area of the different raw materials that will be used to prepare the ammonia sorbent composites. MgCl₂ is a salt in form of crystals as saw in the SEM images at the beginning of the chapter,
this morphology with big particle size and the well packed crystalline structure do not allow the existence of pores, making difficult for small molecules as N\textsubscript{2} to attach to the surface of the material, resulting in a very low specific surface area. In the same way, graphite is a material that presents adsorption layer by layer on a highly uniform non-porous surface, this is due to its special morphology of multiple graphene layers, with a low BET value as is possible to see on the figure. Graphene and SWCNTs are better examples of physical sorbents. Graphene presents a high surface area because its particle size is very small, that allows to the creation of pores in the Nanoplatelets Aggregates, being these pores a perfect site to adsorb small molecules as gaseous nitrogen. Finally, SWCNTs are a material that presents a high concentration of micropores acting as N\textsubscript{2} adsorption sites \cite{64}, a characteristic that is translated in a high specific surface area.

One of the problems that presents the storage of ammonia in salts is its desorption kinetics which, despite reaching high supply capacities, are slow processes that require the use of auxiliary ammonia units to fulfill the demand of reducing agent in the first operating moments of the diesel engines. For this reason, in the present work, it is proposed to improve the sorption kinetics through the combined use of the chemisorption properties of MgCl\textsubscript{2} and the physisorption characteristics of the carbon materials. The main idea when adding graphene or SWCNTs is to provide a greater surface area to the composite, in this way it would be possible to take advantage of the fast kinetics of the physisorption components and the storage capacity inherent to magnesium chloride. In the case of graphite, the intention is more to evaluate its performance as a structural reinforcement for the salt than increasing the surface area of the composite.
Chapter 5

Composites preparation and characterization

Throughout this chapter, it will be presented and discussed the preparation and characterization of the carbon materials/MgCl$_2$ composites. The first section will be centered on the direct mixed composites and characterization by different experiences and techniques; the second section will talk about the composites obtained by the wet impregnation method, as well as its special properties and characteristics.

5.1 Direct Mixed Composites

As described during the Chapter 3, direct mixing method by ball-milling was used to prepare three different compositions of composites graphite/MgCl$_2$ and graphene/MgCl$_2$. For that purpose, the raw materials were putted in the right proportions in bottles along with the mixing beads. In the following section, a deep description of the obtained powders will be carried out.

5.1.1 SEM images and morphology of mixed composites

In Fig. 5.1 it is possible to find as an example two SEM images that correspond to Gt20 and G20 compounds, images for other compositions have been done too, but it will not be presented here for space issues.

Figure 5.1: SEM images of MgCl$_2$ with graphite (a) and graphene (b), Gt20 and G20 respectively.
For Gt20, no reduction of salt particles size has been registered, graphite and salt are not distinguishable but it is assumable that bodies of more than 100 µm correspond to MgCl\(_2\); in general, the salt grains are surrounded by graphite sheets uniformly. In the case of the composite with graphene, change of particle size is easily noticeable, salt crystals in this composite have dimensions of less than 100 µm; in this case, is not possible to differentiate easily the graphene aggregates, because probably they have been reduced into smaller particles and mixed uniformly with magnesium chloride. The differences in the size of salt crystals between both composites may be due to the lubricant effect of graphite during the mixing, ball-milling process can be affected by this characteristic of graphite making harder obtaining uniform mixtures.

### 5.1.2 Tablet pressing and mass retention experiences

For the real application to ASS units, it is preferable to have an ammonia sorbent material with a defined form, i.e. the use of the material in powder form with a low bulk density is not suited for onboard storage [3]. Following this premise, the prepared composites have been pressed into tablet form using a hydraulic press as described in the experimental description. In fact, one of the most important desired features is the improvement of the thermal and mechanical stability of the salt, and the reason for this is to avoid problems as the swelling and agglomeration of MgCl\(_2\), but in the same way, a composite capable to retain molten salt could lead in a better way with possible ammonia condensation at ASS operation conditions (i.e. high pressure and moderate temperatures). To test the behavior of the composites and their mass retention capacity, tablets of \(\sim 8\) mm of MgCl\(_2\) and each composite have been treated at high temperature. The idea with this experience is to evaluate the role of the carbon materials as structural support for the salt. The tablets were treated in a tubular furnace with Ar flow to avoid oxidation, the temperature was increased at 5°C/min from RT to 800°C and kept during 30 min at this temperature.

Images of the tablets of MgCl\(_2\) and composites before and after thermal treatment are available in Fig 5.2, the effect of temperature is obvious for tablets of pure salt or with low content of carbon materials. A tablet of magnesium chloride will melt and lose its form when the temperature arrives to the melting point, but the high viscosity of the molten salt avoid the liquid to spread in the bottom of the container, this is the reason for having this MgCl\(_2\) remaining after the heat treatment in Fig 5.2. The content of carbon materials in the prepared tablets change the behavior near the melting point, graphite and graphene act as a structural reinforcement for the tablet allowing the preservation of the shape, the reason is that these materials allow the molten salt droplets to remain separated in such a way that it is much more difficult for them to flow and move destroying the given shape. It is difficult to know which it the optimal quantity of graphite or graphene that should be added to the composite to avoid melting of the tablet, but a content of carbon materials between 10 an 20% in weight could be enough to preserve the form at high temperature, more experiences with several different contents of carbon material can give a more accurate idea, but it will be not covered in the present work. In the following experiments regarding thermal behavior, only Gt20 and G20 composites will be analyzed as representative composites with carbon reinforcement, even if good results were obtained with lower carbon content.
In order to quantify the loss of mass by the effect of the temperature, more controlled experiments with ~4 mm tablets of the composites with a higher content of carbon materials have been carried out. For that, the tablets were tested in the TGA/DSC equipment from RT to 800°C, but the step at high temperature was removed to protect the machine components. The respective curves can be founded in Fig 5.3 and calculations on mass retention performance have been consigned in Table 5.1. Two different retention percentages are shown in the table: the total mass retention, that takes the initial mass as a reference, and real mass retention, that takes the mass at 400°C as reference. The first one serves to have an idea of how much change the weight of the as pressed tablet, and the second value have into account the release of moisture before 400°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Initial Mass (mg)</th>
<th>Mass at 400°C (mg)</th>
<th>Mass at 800°C (mg)</th>
<th>Total mass retention (%)</th>
<th>Real mass retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gt20</td>
<td>59,207</td>
<td>54,850</td>
<td>52,561</td>
<td>88.77</td>
<td>95.82</td>
</tr>
<tr>
<td>G20</td>
<td>57,370</td>
<td>51,882</td>
<td>48,857</td>
<td>85.16</td>
<td>94.17</td>
</tr>
</tbody>
</table>

The most important information from Table 5.1 is the real mass retention percentage, values of about 95% for both composites are relevant results related to the structural stability of the tablets. In the same way, that 5% of change is the loss of mass due to the formation of MgO and evaporation of molten salt at high temperature, in any case, it is not related to a direct loss of MgCl₂ in the liquid state. This behavior can be explained by two factors: the high viscosity of the molten salt and
the structural support provided by the carbon materials. In fact, the molten salt should have a low fluidity, but the addition of graphite or graphene makes possible for the tablet to stay in a well-defined geometry. Therefore, the proposed composites with content of 20% of carbon material show better performance compared with the pure MgCl\textsubscript{2} regarding stability at high temperature. Problems as the agglomeration of salt and swelling can be countered when structural support is provided by the additives.

Now, it is possible to analyze more information from the mass retention experiences, especially regarding the thermogravimetric behavior of the composites. Fig 5.3 corresponds to the TGA measurements under Ar flow of tablets of Gt20 and G20 from RT to 800°C. Only these two thermograms have been taken because these compositions allow us to understand the role of carbon materials. In both cases, the content of carbon materials is translated into important changes that help to stabilize the composites. The first remarkable difference is the change in the water desorption temperatures for both composites, it is possible to say that the presence of graphene and graphite modifies the global kinetics of the process, and it could be due to the thermal properties of these materials. Another possible explanation is the modification of the mass transport phenomena by two different ways: the reduction of the particle size and the addition carbon materials that could facilitate the release of moisture and other gases from the sample.

![Figure 5.3: TGA/DSC from RT to 800°C of Gt20 and G20 composites.](image)

In theory, the total change of weight in the composites at 400°C should be lower than that of pure MgCl\textsubscript{2}, because more carbon content in the sample means less moisture and HCl release, as in the case of the curve of G20. A decrease of \(~9.5\%\) of the weigh of Gt20 expose one of the problems of the mixture method used in this work, ball-milling process let the moisture in the environment to entry in the mixtures and to form hydrated complexes with the salt; even if the quantity of absorbed water is not that high, it is almost impossible to control this kind of variables, but it could be possible to take preventive measures to avoid this to happen. Another difference between the composites and pure MgCl\textsubscript{2} is the reaction temperature to
form MgO, in the composites, this process starts at \( \sim 450^\circ C \), about 35\(^\circ C\) more than in pure salt, and also the time to achieve a complete conversion is less. The most interesting feature achieved with the addition of carbon materials has been found when the temperature reaches the melting point of MgCl\(_2\). At \( \sim 715^\circ C \) a big change of mass is registered in the salt curve due to the evaporation of molten MgCl\(_2\), but in the composites the change is much more moderate, even at 800\(^\circ C\). This characteristic is a very important improvement regarding thermal stability, a composite that is capable to reduce the losses of molten salt should minimize problems as the accumulation of salt in specific zones of the ASS unit. It is probable due to the additional structural support contributed by the carbon materials making the transport of salt from the liquid to the gas flow more difficult. This behavior has been found in relation with the thermomechanical stability of the composites at high temperature, a characteristic that supports the use of carbon materials as structural reinforcement for MgCl\(_2\).

The tablets used for these mass retention test were studied by SEM as well. Figures 5.4 and 5.5 show the surfaces of the tablets of Gt20 and G20, as well as the effect of the temperature in the top and bottom faces. In Fig 5.4 it is possible to appreciate the distribution of components in both composites. In the case of Gt20, it can be differentiated easily the MgCl\(_2\) from the graphite, the white spots are the salt surrounded by the carbon material; no covering of salt crystals by the carbon material is registered as in the case of the mixed powder discussed previously. G20 is considerably different having into account that only the bigger salt crystals are distinguishable, in the same way as it was appreciated in the mixed powder, graphene covers the majority of the salt surface.

![Figure 5.4: SEM images of the surface of tablets: Gt20 (a) and G20 (b).](image)

The effect of the temperature in the tablets is obvious in both composites. The distribution of salt and carbon materials has been affected as well as the composition of the tablets, something that was rectified by EDS on both surfaces. In Fig 5.5 both faces of the Gt20 tablet are shown, the result corresponds to what was expected. The top face shows a lower concentration of salt than in the tablet without treatment, it is correct having in mind that the molten MgCl\(_2\) went to the bottom of the tablet, something that is confirmed by the bottom face SEM. Similarly, in Fig 5.5 the bottom face of the G20 tablet shows a higher concentration of salt that the top face. The explanation for that behavior is the action of the gravity force on the tablets,
the molten salt goes down causing accumulation at the bottom of the tablet.

In Table 5.2 can be found the information that comes from the EDS measurements, there is possible to see the weigh percentage composition of each face of the composite tablets. In both cases, it was possible to verify the existence of a third compound different of the carbon materials and MgCl$_2$, the high concentration of oxygen in the surface let us know that the formation of MgO has occurred as was expected with TGA experiments under Ar flow.

<table>
<thead>
<tr>
<th>Element</th>
<th>Gt20</th>
<th>G20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top Face</td>
<td>Bottom Face</td>
</tr>
<tr>
<td></td>
<td>Weight%  $\sigma$(wt.%)</td>
<td>Weight%  $\sigma$(wt.%)</td>
</tr>
<tr>
<td>C</td>
<td>30.05  1.74</td>
<td>61.59  2.98</td>
</tr>
<tr>
<td>O</td>
<td>27.79  1.08</td>
<td>11.79  1.45</td>
</tr>
<tr>
<td>Mg</td>
<td>40.89  1.23</td>
<td>7.48   0.77</td>
</tr>
<tr>
<td>Cl</td>
<td>1.28   0.39</td>
<td>19.14  1.71</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Even if the formation of the oxide comes from the initial content of moisture in the sample, the surface of the tablets have been exposed for a longer time to the environment, it makes possible a higher content of water in the exterior, and finally the appearance of more MgO. As it can be checked in Fig 5.2 tablets of
MgCl$_2$ present a kind of shell that appears after the thermal treatment at 800$^\circ$C, it is because the MgO stays after its formation at $\sim 415^\circ$C. On the surface of the composites, MgO looks like deposited dust, but it is in form of particles that come out of the outer part of the tablets. In the same way, Fig 5.6 shows the appearance of the oxide on the surface of a G20 tablet and an EDS mapping in the same zone, as an example of the discussed behavior.

![SEM image and EDS mapping of MgO on top surface of G20 tablet.](image)

The Appendix B corresponds to the detailed EDS mapping in which is possible to appreciate that the white phase has low concentration of chlorine and higher presence oxygen atoms, supporting the presumption of the formation of MgO. In the real application for ASS units, the formation of this compound is not possible because of the operating conditions at temperatures lower than 400$^\circ$C, but it is important to know that reactions like this can occur in case of using these composites in another kind of applications.

### 5.1.3 Specific surface area experiences

As it was discussed before, one of the most important properties with influence in the sorption process is the specific surface area. Materials with physical sorbent characteristics are mainly highly porous materials, as SWCNTs and graphene. In Appendix D, it is possible to find the results of all the BET surface measurements

![BET surface of carbon materials/MgCl$_2$ composites.](image)
that were performed during this work, the values used in Fig. 5.7 representing the influence of mixing MgCl₂ with graphite and graphene, correspond to the average and standard deviation of three experiences for each compound.

Composites with graphite content have a slight increase of the specific surface area, something that is normal having in mind that this carbon material is not highly porous, even so, these mixtures should present an equally slight improvement in the sorption kinetics. In the other hand, mixtures of MgCl₂ with graphene have significant growth of the BET values as can be ascertained in the same figure. A priori, the role of the graphene in the sorption kinetics should be more pronounced than that of graphite. The idea of using porous materials to improve the behavior of magnesium chloride is not only based on the surface area, because materials as graphene will not only provide this characteristic, their porous nature can contribute to the creation of a network of channels and internal tunnels in the composite tablet, thus making it possible to modify the transport of mass inside it. In the same way, materials with the facility to adsorb gaseous species in their surface will provide considerable amounts of the stored compound only by slightly raising the temperature. This theory would allow solving problems of the ASS units as the use of an ammonia auxiliary tank since the part stored by physical means could be extracted as soon as the engine has been turned on. The ammonia adsorption tests allow us to know if this premise is correct, and it will be analyzed in the next chapter of present work.

5.2 Wet Impregnated SWCNTs

Different methods for preparing mixtures of MgCl₂ with carbon nanotubes were considered, but the most appropriate one was the wet impregnation method. Dry methods as direct mixing of SWCNTs with the salt have been discarded because the final composite could have very low bulk density, something that is not desirable for our application. The following section will explain the results obtained for the SWCNTs composites, their behavior under Ar atmosphere, mass retention and other features that have been discussed for the graphene/graphite composites as well.

5.2.1 Preparation of composites

The impregnation method was explained in chapter 3, two different saturated solutions of MgCl₂ were used and the final SWCNTs composites had considerably different final salt contents. In the Table 5.3 it is possible to check the difference in the final content of salt in both composites, this can be explained by the differences in the solution. The salt used in this work is highly soluble in water and moderately soluble in ethanol, then the first solution (pure water as solvent) had more content of dissolved MgCl₂ than the second solution (half water and half ethanol, in

<table>
<thead>
<tr>
<th>Material</th>
<th>Solution (% v.)</th>
<th>Initial SWCNTs (mg)</th>
<th>Impregnated SWCNTs (mg)</th>
<th>MgCl₂ content (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>100% H₂O</td>
<td>106,0</td>
<td>170,1</td>
<td>37,7</td>
</tr>
<tr>
<td>C2</td>
<td>50% H₂O/50% Ethanol</td>
<td>103,5</td>
<td>378,2</td>
<td>72,6</td>
</tr>
</tbody>
</table>
volume). Then, it can be easy to think that the impregnation in the first solution would produce composites with more final salt content, but the results show the opposite. During the preparation of both solutions, it was possible to verify that it is a highly exothermic process.

The explanation for a final content of 72.6% of salt in the C2 composite is the nature of the solution. From the experimentation, it was possible to verify that the solution using pure water as a solvent has a low viscosity, and the solution with a mixture of water/ethanol was more viscous. In the same way, the dispersion of SWCNTs during the impregnation was different, in the second solution it was possible to see a complete distribution of the carbon nanotubes in the total volume; instead, in the first solution, the carbon material was easily precipitable. From the literature, it was possible to determine that the viscosity of the second solution can be done to the existence of MgCl$_2$–alcohol adducts as well as hydrated complexes. In fact, magnesium chloride dissolution equilibrium in ethanol aqueous solutions is given by [65]:

$$\text{MgCl}_2 \cdot 6 \text{C}_2\text{H}_5\text{OH}(s) \leftrightarrow \text{Mg}^{2+}(\text{aq}) + 2 \text{Cl}^-(\text{aq}) + 6 \text{C}_2\text{H}_5\text{OH}(\text{aq}) \quad (5.1)$$

Then, having in mind the formation of this big MgCl$_2$–alcohol complex, it is possible to say that SWCNTs could interact with it, forming a wet composite with a high content of salt, as well as water and ethanol. After filtration and drying, no alcohol adducts will rest as part of the composite. As a matter of fact, ethanol could act as a dehydration agent in the same way that other alcohols have been used as organic solvents for the dehydration of hydrous magnesium chloride [66]. In that way, a higher content of MgCl$_2$ is possible in the C2 composites. Here, refer to "MgCl$_2$ content" is not saying a "pure content" of that salt, because alcohol and hydrated complexes are formed during the solution method, the retained chloride after drying is a combination of pure salt with a high percentage of hydrated complexes. Later on, it will be discussed with the help of the TGA/DSC experiences. As the final content of salt for the C1 composite is not enough to think about an application to ammonia storage systems, in the following experiences only the C2 composite will be tested, hoping that it will have interesting results as a sorbent material for ASS units.

5.2.2 SEM images, EDS and morphology

To verify the morphology of the obtained composite, SEM images were taken. In Fig 5.8 two images at different magnification can be found, it is possible to see that C2 composite is formed by an intricate network of carbon nanotubes with MgCl$_2$. In the image at higher magnification, it is possible to see that the nanotubes are covered by a layer of salt, similar to snow covering the branches of the trees. From the physical consistency of this composite, it is possible to say that the nanotubes act as a support that is taken by the salt as a structural reinforcement. In fact, among all the mixtures studied in this work, C2 is the one that has a more intimate interaction between the carbon material and the magnesium chloride; this can be an important feature in terms of stability and mass retention, something that will be verified in following experiences. From Appendix C, where it can be appreciated
an EDS mapping on a sample of C2 composite, it is possible to confirm the presence of Mg, O, Cl and C, as well as some Fe atoms (from the SWCNTs impurities); as discussed before, the preparation method by wet impregnation allows the formation of hydrated complexes that remain in the sample even after the drying, and this is the reason for the presence of oxygen in the sample. Interestingly, the presence of carbon is low compared with magnesium, showing that the salt covers almost all the surface of SWCNTs, making difficult the detection of this element.

The preparation of tablets for the C2 composite was done in a different way that for the mechanically mixed composites. In this case, the wet product obtained after filtering was molded in the form of 8mm diameter tablets with the help of the die used to prepare tablets previously, no pressure greater than that which can be supplied by the action of tightening the movable parts of the die was used. This strategy was used to have easy-to-use tablets for mass retention tests, the problem is that these composites do not have the same final amount of salt as the composite without a defined form, this is due to the fact that in the pressing process there is loss of solution and finally less MgCl₂ is present in the tablets. However, the obtained green bodies were used for the mass retention test in order to have an idea of the thermal behavior of that composite. In Fig 5.9 it is possible to see the surface
of a tablet of C2. In the same way as the last SEM images, an intricate network of SWCNTs with salt can be appreciated. It is clear that the content of MgCl$_2$ is lower than in the case of bulk composite, but for the following experiences it must meet the expectations.

5.2.3 Mass retention and thermal stability

Similarly, a mass retention test was carried out on an 8 mm tablet to check the improvement of thermal and structural stability. The same heat treatment was used from previous experiences, and the images taken are in Fig. 5.10. The first fact to highlight is the change of color of the composite sample C2, the tablet after 800°C takes a lighter color than the initial, this is probably linked to the production of magnesium oxide at temperatures close to 415°C. The formation of this compound is much more representative than in the case of graphite and graphene composites because all the salt has passed through the hydrated state. It is also important to note that there is no loss of salt in the form of liquid since the surroundings of the tablet were found clean of traces of molten MgCl$_2$.

To confirm what happens during the mass retention test, a TGA/DSC with the same conditions was performed on a sample of bulk C2, and the curves are presented in Fig. 5.11. From these experiences, it was possible to calculate the total mass retention of 62.25% and the real mass retention of 86.32%. The first value is the reflection of the total mass loss during the whole experiment, which makes sense when taking into account that this composite undergoes changes in the mass
due to the water and HCl release of the reactions involved with the increase of temperature. It is possible to notice that the endothermic peaks related to water desorption reactions and MgO formation are larger than the peaks found for pure MgCl$_2$, which verifies that the moisture content in the composite is much higher than in the raw material. The value of real mass retention is lower than the percentages calculated for G20 ant Gt20, this also agrees with a greater release of water and HCl in the reaction at $\sim$415°C. The melting point was found at approximately 715°C, in the same way as for pure salt, the main difference is that the peak is less significant which means that the salt content in its pure form is much lower than expected, but anyway, the content of SWCNTs acts in a similar way as for the composites previously studied, since there is no significant loss of mass in the vicinity of the melting point. The carbon nanotubes also have the role of structural support that helps to avoid mass loss due to the fusion of MgCl$_2$.

5.2.4 Specific surface area experiences

According to the surface area measurements and the calculations given in Appendix D, the surface area of the C2 composite is $100.28 \pm 17.07$ ($m^2/g$), this agrees with the expectations of an intermediate behavior between that of it’s components. As already said from the images of SEM, the carbon nanotubes offer a structure for the magnesium chloride to be reinforced, but also allows the creation of pores and cavities that did not exist before. Probably, the C2 composite will present a physisorbent character much more marked than that of the other compounds due to the intimate mixture between the nanotubes and the salt. This will be verified in the next chapter, in which the sorption experiences of MgCl$_2$ and all prepared composites will be analyzed. In the same way, it will see discussed the influence of characteristics such as the existence of pores and high surface area in the kinetics of the ammonia storage and release processes.
Chapter 6

Ammonia storage performance

The present chapter is the compilation of all the ammonia sorption experiences performed during this project, including the complete characterization of MgCl₂ and the comparison of the different composites prepared for the application to ASS units. Different experiences performed to understand the absorption/adsorption behavior, the desorption kinetics and the role of the carbon materials will be presented in this part of the report. The experiences performed here followed the procedure explained in Chapter 3, but the results have been treated and presented in figures to make easier to understand the performance of the sorbent materials.

6.1 Ammonia storage characterization of Magnesium Chloride

In this section, the ammonia sorption and desorption process of MgCl₂ will be explained in depth. As it was discussed in the background chapter, magnesium chloride is metal halide that can absorb six molecules of ammonia per molecule of MgCl₂, this process is divided into three different chemisorption steps showed in Equations 2.11, 2.12 and 2.13. In that way, ammonia is stored safely in the form of metal ammine complexes with the formula Mg(NH₃)ₙCl₂ with n = 6, 2, 1, reaching considerably high absorption capacities. In the first graphic of Fig 6.1, it is possible to find the TGA/DSC curves of the ammonia absorption process of MgCl₂ at 25°C and 1 bar, with an ammonia flow of 100mL/min. From the DSC curve, it was verified that the ammonia absorption reactions are exothermic, something that makes difficult an isothermic process in the equipment used for these experiences. In fact, the absorption temperature in all the experiences is around 25°C, with positive fluctuations of up to 3°C. From the TGA curve, it was calculated an Ammonia Storage Capacity of 58.96 mmol of NH₃/g of Mg(NH₃)₆Cl₂, lower than the theoretic capacity of 63 mmol of NH₃/g of Mg(NH₃)₆Cl₂. The difference is due to the content of moisture in the initial sample, that is translated into MgOHCl content when the degassing is performed at 400°C before the absorption experience. As the aim of this work is to analyze the effect of the addition of carbon materials in the sorption kinetics, the presence of should not be of an inconvenience.

According to the TGA/DSC curves, the absorption of the two first molecules of ammonia is carried out during the first 70-80 s of the process, it is represented by the big exothermic peak and ammonia sorption of ~33% of the final capacity. This agrees with what was expected for the process, taking into account that the absorp-
Figure 6.1: Ammonia sorption behavior of MgCl$_2$: absorption (up), desorption under Ar (middle) and desorption under NH$_3$ (down).
tion reactions of the first two molecules together have a higher enthalpy of reaction than the third step. Likewise, the first two stages of absorption are faster processes because they involve a smaller total mass transfer, which is explained by an abrupt mass change in a short time and the superposition of the two exothermic peaks forming a larger one. Subsequently, the process becomes slower and the storage of the four remaining parts of ammonia develops in a much longer time, passing the 1300 s of total duration, and the heat release is also reduced as the process finishes.

The desorption of ammonia was studied under two different atmospheres, the reason for this is based on the operating conditions of a real ASS unit. First, when the engine is turned on, the ASS tank contains ammonia in the form of metal ammine complexes, at low temperatures the ammonia partial pressure is close to zero. When the temperature of the tank begins to increase, the process of desorption of ammonia starts and the partial pressure of NH₃ increases equally, following the Clausius–Clapeyron equation shown in Eq [2.8]. Then, to emulate the desorption process under conditions similar to the real ones, two different experiences were evaluated for both MgCl₂ and the prepared composites. The first experience is desorption under Ar flow at different temperatures, and the second one, desorption under NH₃ flow with increasing temperature until 200°C and then a change of atmosphere to Ar. The complete description of the experiences can be founded in Chapter 3. The two desorption curves presented in Fig 6.1 correspond to the TGA and the evolution of the temperature during the experiences.

During the desorption under Ar (graphics in the middle), it was verified that ammonia can be released from MgCl₂ ammine complexes at different isotherms (35, 60 and 200°C), even if the interest of this project is centered in the first minutes of the desorption. It is interesting to see that the desorption process has different release rates at different temperatures, according to what was expected and knowing that there are three different equilibrium. During the isotherms at 35 and 60°C, the desorption process corresponds to the reaction from six to two molecules with an ammonia desorption percentage of ∼65%. During the next step from 60 to 200°C, all the ammonia stored in form of Mg(NH₃)₅Cl₂ is liberated, and a small percentage that remains in the sample can be probably released at slightly higher temperatures. The desorption process under NH₃ shows that low quantities of ammonia are released when the atmosphere is saturated by the same gas, only when the temperature arrives at ∼142°C the first four parts of NH₃ went out of the MgCl₂ complex, showing a similar ammonia desorption percentage of ∼65%. Then, the change of atmosphere is registered at 1700 s, it first generates fluctuations in the temperature and then, an extra amount of the gas is released, something that would happen when the ASS unit is almost empty.

From the experiences, it was also possible to verify the expansion phenomenon typical of this process. During absorption, the volume increases considerably due to the entry of ammonia into the salt, a behavior that seeks to be avoided but due to the nature of the process is very difficult to achieve. In the same way, during the desorption process, a large number of pores is found due to the release of the ammonia molecules from the complex, something that had also been previously recorded in other studies with MgCl₂ [67].

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6.2 Ammonia storage performance of carbon materials composites

In this section, the results of the ammonia sorption/desorption tests are presented and compared. No distinction will be made between composites prepared by mechanical mixing or by wet impregnation, even if the mechanisms involved may be slightly different, the final application and the desired performance are the same for any type of sorbent material that may be used, allowing us to compare them.

6.2.1 Ammonia sorption performance

The ammonia sorption experiences in carbon materials/MgCl$_2$ composites have been performed in the same way than in the case of the pure salt. After degassing at 400°C, the samples were cooled until 25°C and the ammonia flow was passed isothermally. In the Fig 6.2, two different representation of the sorption process can be founded. The first one plots the ammonia sorption capacity in each moment of the experience, the second figure shows the ammonia sorption percentage (ASP), it is a normalized quantity that makes easier the comparison of the kinetics between the different samples. The ASP is calculated as follows:

$$ASP = \frac{m - m_0}{m_s - m_0}$$ (6.1)

where $m$ is the mass in every instant, $m_s$ is the mass at the saturation point and $m_0$ is the initial mass of the sample. Together these two figures allow understanding the role of the carbon material on the sorption behavior of the composites.

In the first figure, the main fact that is possible to see that all the composites have lower total ammonia capacity than the pure MgCl$_2$, this is something that follows the expectations because of the well-known storage capacity of that salt. As discussed in Chapter 2, the chemical sorption mechanism allows metal halides to have higher NH$_3$ capacities, and no physical sorbent will beat this feature. The next interesting point regarding directly mixed composites is the slight difference between the total sorption capacity between both kind of composites, graphene composites have higher ammonia storage than the graphite ones. This difference can be explained by the difference in the specific surface area of both carbon materials, a behavior that was expected because of the physical sorption contribution of a highly porous material as graphene. In the other hand, C2 composite has the worst ammonia sorption capacity, but it is explained by the low final content of MgCl$_2$ in the composition, making difficult an outstanding result in this aspect.

The second figure gives a better and more clear idea about the role of the carbon material in each composite, the ASP values show how fast the composites arrive at the saturation. In all the cases, the composites show faster sorption than the pure MgCl$_2$, especially the samples with a high specific surface area. The explanation for this behavior has two main reasons: the physical sorption mechanisms and the creation of tunnels that facilitate the transport of ammonia. The physisorption mechanism can improve the storage rate in the first minutes of contact with the NH$_3$ flow, a feature that is sawed in these composites, more clearly for the graphene
composites and SWCNTs, but it is an effect that does not allow an improvement throughout the entire storage time. That is why the explanation of the creation of tunnels is a stronger reason, the improvement in kinetics is seen mostly in composites with high surface area, but it is important to consider that this characteristic is typical of highly porous materials. The addition of this kind of materials allows the creation of a system of paths in and out of the composite principally consisting of MgCl$_2$, making it easier to transport gaseous ammonia mass. In the case of pure salt, the molecules of ammonia have to travel inside the crystals through paths with more obstacles; but in the prepared composites, the NH$_3$ molecules go into the samples via the system of tunnels and forms ammine complexes with MgCl$_2$.

In general, all the analyzed composites have better sorption kinetics than pure magnesium chloride, but those who have graphene and SWCNTs get faster to saturation. In the actual application to ASS units, this would translate into shorter
tank filling times, making the process more efficient and saving time that could be used to transport people or cargo.

6.2.2 Ammonia desorption performance

As explained above, the desorption was evaluated under two different atmospheres to better understand what happens when the ASS unit is cold and when it has reached higher operating temperatures. This is why in Fig 6.3, two different graphs are presented, one for Ar atmosphere and another for ammonia atmosphere. In the same way, as for the process of taking ammonia, a normalized value called ammonia desorption percentage (ADP) is calculated to more easily understand the kinetics of the desorption process. The formula used this calculation is:

\[
ADP = \frac{m_s - m}{m_s - m_0}
\]  

(6.2)

where \(m\) is the mass in every instant, \(m_s\) is the mass at the saturation point and \(m_0\) is the initial mass of the sample, these two last values are taken from each sorption process and before the desorption experience.

The experience of releasing ammonia under Ar atmosphere allows us to easily see how carbon materials influence the desorption process. In this case, it is possible to notice the effects of the physical mechanism of desorption, making the prepared composites to have better performance than pure salt. In general, it could be said that the same reasons may explain the improvement in this test: physisorption and tunnels formation. During the process of release of ammonia, the physical mechanisms are more important, contrary to what has been witnessed during the ammonia uptake. If there is a low or no partial ammonia atmosphere, the carbon materials are the first to provide the reducing agent, which is why during the first 150s of experience, it is seen how materials with a high surface area can supply more NH\(_3\).

After these first moments with notable differences, mainly for graphene composites, the release rate is more or less constant in all cases. It is important to note that the differences in the range of 0 to 300 s are really significant, after this time, pure MgCl\(_2\) has released \(\sim 3.4\)% of the total ammonia stored, and materials as the graphene composites a quantity of \(\sim 5\)%.

The second graph in Fig 6.3 shows the evolution of ADP under ammonia atmosphere and as the temperature increases at a speed of 10°C/min, this test highlights the chemical mechanisms of desorption since an atmosphere saturated with NH\(_3\) does not allow materials with physical desorption characteristics to easily release the stored gas. It can be verified that in all cases of directly mixed composites, the behavior is almost identical to that of pure MgCl\(_2\); low percent release at low temperature occurs, but when it approaches \(\sim 142^\circ\)C, the discharge of the first four ammonia molecules occurs. In the case of the actual application, this means that when the tank is approaching high temperatures, the most important mechanism is the chemical one, since the small amount of physically stored NH\(_3\) has already been supplied.
A special case is the composite C2, it is seen that throughout the whole experience, different mechanisms to those of pure MgCl₂ are involved, and there may be two main reasons for this. The first is the intimate mixture between SWCNTs and the salt, allowing a high porosity in the composite, not only due to the addition of the carbon material but also because of the pore creation in the saline phase. The second is the existence of MgOHCl that could modify the kinetics of the absorption reactions. The effect of this compound in large quantities such as those present in this composite is not well known, but it is likely that its participation generated the changes observed during these tests. Finally, it is likely that other properties such as the thermal conductivity of carbon materials could affect the sorption and desorption process in composites, for this it would be necessary to check if this has been modified. An improvement in the thermal properties could also explain the slight increase in sorption and desorption velocities during the first instants of the experiences.
Chapter 7

Conclusions and Perspectives

Conclusions

- It has been possible to prepare magnesium chloride composites with different carbon materials like graphene, graphite, and SWCNTs, with losses of total ammonia storage capacity, but significant improvements in other key properties for the target application.

- The addition of carbon materials helps to strengthen the MgCl$_2$, making possible composites with better resistance to temperature and high mass retention capacity.

- Porous materials such as graphene and SWCNTs make possible the combination of the physical and chemical mechanisms of sorption, enabling the improvement of ammonia sorption rate and desorption rate under Ar atmosphere. The creation of a system of tunnels and channels facilitates the transport of ammonia in and out of the composite, in this way higher sorption/desorption speeds are achieved.

- Basic problems of chloride salts as swelling and agglomeration can be overcome thanks to the capacity to retain mass and shape of the composites prepared in this work.

Perspectives

- Changing the carbon content between 10-20 wt.% could reduce the decrement of storage capacity while preserving structural improvement and stability.

- The process of mixing by ball milling can be changed by a more suitable method for this kind of materials so that the absorption of moisture from the environment can be avoided and more uniform mixtures can be obtained.

- The preparation process of composites with SWCNTs can be modified in multiple variables such as solvent, the concentration of salt in the solution, drying temperature and quality of carbon nanotubes; it is possible to obtain better results of MgCl$_2$ content.

- Perform sorption tests with multiple cycles to evaluate the long-term behavior, as well as experiences at higher pressures similar to real ASS unit conditions.
Appendix A

SWCNTs impurity detection

Figure A.1: EDS electron image (a) and spectra (b).
Appendix B

Detection of MgO on G20 surface

Figure B.1: SEM/EDS element mapping on G20 top surface.
Appendix C

Element mapping on C2 composite

Figure C.1: SEM/EDS element mapping on SWCNTs/MgCl$_2$ composite.
# Appendix D

BET surface results for raw materials and composites

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Table D.1: BET surface results and calculations.
Bibliography


