In situ regenerable air purifiers

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Nicht Sieg sollte der Sinn der Diskussion sein, sondern Gewinn.

(Joseph Joubert)

If you think you can do a thing,
or if you think you can’t do anything, you are right.

(Henry Ford)
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I want to take this special opportunity to express my deepest gratitude to all the people that played an important role, consciously or unconsciously, in this journey that personally started a long time ago. Looking back, this PhD is for me the culmination of a project started over 15 years ago. During this time many ups and downs have alternated themselves. Fortunately, I was always lucky to find people on the way from various fields, supporting and helping me to never give up. To those who believed in me is this theses dedicated.

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Zusammenfassung


Die katalytischen Eigenschaften von Ceroxid (CeO₂) für die Verminderung von Luftverschmutzungen führten zur Entwicklung des sogenannten Drei-Wege-Katalysators für die Reinigung von Autoabgasen. Die Säure/Basen- und Redox-Eigenschaften der Oberfläche von Ceroxid, zusammen mit seiner ausgeprägten Sauerstoffmobilisität, haben uns dazu inspiriert dieses Material als bifunktionaler Luftreiniger für saure organische VOCs zu verwenden. Diese bestimmte Klasse von VOCs beinhaltet kurzketttige, übelriechende Fettsäuren, welche entweder direkt vom Menschen oder Tier abstammen oder durch Oxidationsvorgänge im Innenraum entstehen können. In einem ersten luftreinigenden Schritt, wurde ein saures VOC (Hexansäure), bei Raumtemperatur adsorbiert. Im darauffolgenden regenerierenden Schritt wurde das
übelriechende VOC katalytisch hauptsächlich zu CO$_2$ und Wasser oxidiert ohne es dabei wieder in die Umgebung freizulassen. Dieser Ansatz wird in Kapitel 2 präsentiert.


Kapitel 5 fasst die Resultate zusammen und diskutiert die Ergebnisse dieser Arbeit. Eine kritische Hinterfragung soll die Resultate in einem grösseren Zusammenhang stellen, vor allem hinsichtlich Sicherheit, Anwendungsgebiet und Herstellung der untersuchten Systeme.
Summary

Our modern live style has led us to spend more than 80% of the time indoor. Therefore enormous amount of energy is needed to reach and maintain todays indoor air quality standards. Since the global population is constantly growing and the energy production has still a remarkable environmental impact, a more sustainable way for indoor air purification is demanded. As a consequence more energy efficient air purification methods are required. Volatile organic compounds (VOCs), found in indoor air, have been recognized to be potentially harmful to humans and need to be controlled. The here presented thesis indicates energy efficient and sustainable alternatives to currently used strategies for indoor air purification, based on the principle of adsorption and in situ regeneration by total oxidation of the captured VOCs.

Chapter 1 is divided into five sub-chapters. A first point discusses the importance of clean air for people. After a brief historical outline on air pollution, threats associated with it are mentioned. Additionally, various sources of indoor air pollutants with particular emphasis on VOCs are discussed. The most popular technique to maintain a clean and comfortable indoor climate are heating ventilating and air conditioning systems (HVAC). Associated problems with HVAC are briefly reviewed. Alternative methods for removal of VOCs such as thermal- and catalytic oxidation, condensation, absorption and adsorption are briefly presented. In the last three sub-chapters the materials investigated in this thesis i. e. activated carbon, zeolites and cerium oxide nanoparticles are discussed with regard to their application in air purification.

The catalytic properties of ceria based materials have contributed to the implementation of the three-way-catalyst in automotive engines for air pollution mitigation. The acid/base and redox properties of the cerium oxide surface, combined with an excellent oxygen mobility, has inspired us to use this material as a bi-functional air cleaner for the removal of malodorous acidic organic VOCs. This class of VOC is represented by small fatty acids, deriving either directly from humans, animals or from indoor oxidation processes. In a first air purification step an acidic VOC (hexanoic acid) was adsorbed at room temperature. In a subsequent regeneration step the captured air pollutant was catalytically oxidized mostly to CO$_2$ and water without being released to the atmosphere. This work is presented in chapter 2.
Indoors VOCs may vary in size, polarity and reactivity. Hence, not all compounds can be captured and combusted at the same time by CeO$_2$, as it was the case for acidic organic VOCs. CeO$_2$ was combined with an adsorber material, able to capture a greater variety of VOCs, and suitable for in situ regeneration. Chapter 3 presents the findings made using physical mixtures prepared from common zeolites, such as ZSM-5 and 13X, as adsorption and capture unit, and cerium oxide, as the oxidative catalyst. The adsorption/capture and release/oxidation process (ACROP) was investigated by using five different VOCs.

One of the most well-known filter materials is activated carbon (AC). It can be used in households in the kitchen ventilation or even in aquaria, for water purification. AC can be used as a medication too, if a poisoning compound is ingested and needs to be captured before it is absorbed by the body. All these different application can be traced back to the outstanding adsorptive properties of AC. Due to the extremely high surface area of more than 1000 m$^2$/g, and the mostly lipophilic character, most organic substances are strongly adsorbed on AC out of liquids or gases. However, in most domestic applications the spent AC filter is simply replaced by a new one. Only for large facilities that use significant amounts of AC, regeneration in specialized plants is economically feasible. For domestic applications, however, an in situ regeneration of spent AC would be more sustainable, both environmentally and economically. Chapter 4 presents the results of such a process. AC was loaded with VOCs and regenerated thermally in air. The desorbed VOCs were subsequently oxidized to CO$_2$ and water, on a serially mounted CeO$_2$/TiO$_2$ catalyst bed.

Chapter 5 summarizes and discusses the findings of this thesis. The findings are critically reviewed in a broader perspective regarding safety issues, application and production.

Chapter 6 proposes future applications and strategies in the field of air purification. A scale up of the activated carbon set-up is suggested. Moreover, the removal of formaldehyde using zeolites and a multifunctional in situ regenerable adsorber for various types of VOCs is presented. Finally, a possible implementation of the studied systems in a four story building is discussed.
1. Introduction

1.1. The importance of clean air

On average people breathe about 16 times per minute. In a day this corresponds to about 23,000 in- and exhalations. Assuming an average inhalation volume of 0.7 L this would correspond to about 16 m$^3$ of air circulating through our lungs [1]. Consequently, as we spend on average almost 20 h per day in closed rooms, our health is mostly affected by indoor air quality (IAQ) [2]. Ideally the air that we breathe contains 21 vol. % of oxygen, 78 vol. % of nitrogen and 1 vol. % of trace gases such as argon, water, CO$_2$ and other minor components. Unfortunately, these minor components may represent air pollutants (APs). Since research indicates that APs concentration is higher indoors than outdoors much attention to IAQ has to be given [3].

1.1.1. History of air pollution

The exposure of people to indoor APs, and the associated threats, can be traced back to the time when humans sought protection in caves. In fact, soot found on the ceiling of ancient caves clearly shows a high level of air pollution, deriving from open fires used for cooking or warming [3, 4]. Even in ancient times, the Greeks and Romans were concerned about polluted air, but much later, only in the 18$^{th}$ century, IAQ, or more precisely “bad indoor air quality”, was tackled seriously by a number of scientists. For instance, Gauger (1714) concluded that “bad air” was responsible for the spreading of illnesses [2]. Remains from such theories can still be found in the word of the infectious disease “malaria”, which in fact means “bad air”. Later, Pettenkofer (1818 – 1901) investigated the “bad air” problem more systematically and concluded that unpleasant sensations of stale air in rooms were not because of humidity, heat, carbon dioxide or oxygen deficiency, but rather the presence of other organic compounds, emitted from the human skin and lungs while sweating and breathing. Based on this research several studies were made during the end of the 19$^{th}$ and the beginning of the 20$^{th}$ century that searched for toxic effects of organic substances in expired air, the “anthropotoxines”. However, no such “anthropotoxines” were found and the reason for discomfort in indoors was attributed to the warmth of crowded rooms and malodorous body exhalations. To overcome this discomfort, ventilation seemed to be appropriate, as the main source of indoor air pollution was attributed only to the humans body perspiration [2].
1.1.2. Threats to human health

Although we know better nowadays, indoor air has a higher pollution level compared to environmental air [2]. People in developing countries face serious problems with indoor air pollution [2, 5]. There, it is common to burn biomass in unvented rooms, hence, exposing surrounding people to high concentration of particulate matter and carbon monoxide, among other combustion side products. This exposure results in a number of negative health effects such as acute respiratory infections (ARI), chronic obstructive pulmonary disease (COPD) and lung cancer [6]. Almost 2 million people worldwide die per year as a consequence of this form of indoor air pollution. A simple vented stove could save many lives. Also in developed countries, a strong connection between indoor air quality and negative health effects such as cancer, allergies, sick building syndrome (SBS), multiple chemical sensitivity and ARI can be made [2, 7]. Nonetheless, there is no evidence for single APs being linked to an increased health risk. More research identifying the relevant risk indicators is required [2].

1.1.3. Sources for indoor air pollution

There are various indoor air pollutants (IAPs). These might be linked to activities of occupants (e.g. smoking), combustion processes (e.g. oil heating) or emissions from the building itself [3]. Emissions from buildings (Figure 1.1) can be divided in short term and long term emissions. Short term emissions may originate from manufacturing components which may liberate volatile organic compounds (VOCs). These VOCs comprise among others paints, varnishes, solvents or wood preservatives [3, 8, 9]. These emissions are expected to diminish drastically within 6 month to one year after completing the building. Long term emissions, however, derive from factors affecting the materials present in the building. These factors might be moisture, acids, bases or chemicals. High temperature or sun irradiation may also be considered. These long term emissions are seen as major health concern [2, 7]. Air pollution can also have biological origins. Biological sources include allergens originating from pets, fungi (spores), bacteria or viruses. Non biological APs include hydrated silicates (asbestos), CO₂, CO, SO₂, NOₓ, radon, particulate matter and the afore mentioned VOCs such as formaldehyde and polycyclic aromatic hydrocarbons (PAHs) [3, 10]. Outdoor air can also be a source for IAPs, especially for buildings situated in urbane or industrialized zones.
The concentration of indoor air contaminants can be influenced by ventilation rate (open windows), production rate of single APs, available air volume and passive removal by adsorption on surfaces or absorption in liquids [3, 10, 11]. Table 1.1 summarizes some IAPs and possible sources from outdoor.
### Table 1.1 Major indoor pollutants and emission sources

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Major emission sources</th>
<th>% from industry b</th>
<th>% from transport b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allergens</td>
<td>House dust, domestic animals, insects</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Asbestos</td>
<td>Fire retardant materials, insulation</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Metabolic activity, combustion activities, motor vehicles in garages</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>Fuel burning, boilers, stoves, gas or kerosene heaters, tobacco smoke</td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Particleboard, insulation, furnishings</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Micro-organisms</td>
<td>People, animals, plants, air conditioning systems</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>Outdoor air, fuel burning, motor vehicles in garages</td>
<td>38</td>
<td>49</td>
</tr>
<tr>
<td>Organic substances</td>
<td>Adhesives, solvents, building materials, volatilization, combustion, paints, tobacco smoke</td>
<td>52</td>
<td>34</td>
</tr>
<tr>
<td>Ozone</td>
<td>Photochemical reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particles</td>
<td>Re-suspension, tobacco smoke, combustion products</td>
<td>56</td>
<td>25</td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons</td>
<td>Fuel combustion, tobacco smoke</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pollens</td>
<td>Outdoor air, trees, grass, weeds, plants</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Radon</td>
<td>Soil, building construction materials (concrete, stone)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fungal spores</td>
<td>Soil, plants, foodstuffs, internal surfaces</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>Outdoor air, fuel combustion</td>
<td>90</td>
<td>2</td>
</tr>
<tr>
<td>Lead</td>
<td>Leaded aircraft fuel, incineration plants</td>
<td>31</td>
<td>60</td>
</tr>
</tbody>
</table>


Volatile organic compounds are considered to be an important class of indoor APs. These compounds are classified having a boiling point between 50 °C and 260 °C [10]. Some VOCs found indoors may be just malodorous compounds that need to be removed for maintaining a pleasant environment or, they may represent serious threats for human health if people are exposed for a prolonged time. Malodorous substances originating from humans may include short chain fatty acids, sulfides or amines (e. g. trimethylamine, fishy odor). Some other compounds deriving form humans are summarized in Figure 1.2:
More than 350 VOCs with a concentration higher than 1 ppb (part per billion) have been found indoors [12]. Indoor VOCs concentration levels are mostly below odor threshold but they are still several times higher than outdoor levels [13]. Exposure to VOCs can lead to chronic or acute health effects depending on the individual susceptibility and health history [3]. Some of these VOCs are frequently found as flavor additives in cosmetic or cleaning products (Figure 1.3). Additionally, as there is increasing evidence that many chemicals react in air or on surfaces in the indoor environment, dangerous side products such as formaldehyde needs to be considered as well [14-16]. Possible reactions including ozone and VOCs may produce such APs [17-19]. Ozone can be formed outdoors through sun irradiation on smog and subsequently transported indoors or may be generated indoors through electrical discharge in a simple laser printer.
As mentioned before, a common way to keep good indoor air levels is to ventilate. The main aim of ventilation is to dilute and remove the APs. As a result for increasing energy prices, environmental preservation and the public awareness upon energy crisis like the one in the 1970s, ventilation rates have been reduced in western countries. Buildings have been designed by considering the need for energy efficiency, hence, possibly influencing negatively the incidence of allergies caused by APs [2, 3, 20]. Exchange rates below 25 l/s and person in public buildings are associated with higher risk for SBS. This affects the well-being of employees and the productivity more than some major diseases [2, 7, 21]. The SBS includes mucosal, skin and general symptoms related to the working place [22]. SBS symptoms are found to be more common in modern energy-efficient and airtight buildings, particularly when heating, ventilation and air conditioning systems (HVAC) are installed [3, 21].
1.2. Efforts to get clean air

1.2.1. Costs for clean air

The world economies are growing at a rate of 1% for developed countries to almost 4% for China. With almost 1.4 billion people is China the largest country in the world by population. In parallel to population growth also the energy demand is growing. Among industry and transport, residential and commercial buildings account now for 20 to 40% of the global energy demand. Reasons for this increment can be found not only in growing populations but also in the need for high comfort levels, as people spend most of their time indoors. The spreading of building services such as HVAC (Figure 1.4) is a main driving force for this development. This accounts for about 50% of the building energy consumption which is more than domestic hot water production and lighting and corresponds to 10 – 20% of the total energy consumption in developed countries [23].

1.2.2. Heating ventilating and air conditioning systems

To meet the required standards, HVAC systems are extensively used in public buildings such as schools. The US Environmental Protection Agency (EPA) has outlined design tools for proper indoor air quality supply via HVAC systems. The selection of HVAC equipment is based on many factors, including heating and cooling needs, energy efficiency, humidity control, potential for natural ventilation, outdoor air quality, indoor air quality and costs. Figure 1.4 shows schematically a HVAC system. In order to keep the costs as little as possible, energy recovery is required. This can be achieved by using heat exchanger and natural convection using e.g. vertical/thermal displacement ventilation [24]. The location for the outdoor air supply and exhaust must also be chosen carefully in order to minimize problems associated with blockage of airflow and inflow of contaminated air from the outside. Even the grilles, protecting the air intakes, should be bird- and rodent-proofed to prevent piercing, roosting, and nesting. The outdoor air must be filtrated before being flushed into the building. Filtration removes dust, airborne particulates such as pollen, mold spores, animal dander, insects, VOCs and infectious bacteria. The filters must be chosen carefully in order to achieve good levels of purification. Additionally, pressure drop and costs should be minimized. Removal of VOCs is sometimes achieved via permanganate oxidizers and activated charcoal filters [25]. Moisture accumulation, originating from excess moisture in outdoor air or condensation droplets from cooling coils, is a problem that has to be controlled, as damage to the building may occur. Additionally, mold growth, which can also lead to health problems for resident, must be
prevented. Finally, humidity accumulated in the ventilation system may allow growing of bacteria that produce malodorous VOCs.

**Figure 1.4:** Heating ventilation and air conditioning system (HVAC). Fresh air coming from outside needs to be pumped, filtered, cooled or heated. A fraction of the indoor air is exhausted after being consumed. If no heat exchanger is installed, heat energy can be lost especially during the cold season (adapted from: http://www.zelenabuducnost.sk).

The picture described on HVAC systems displays a number of problems that have to be considered. This is also because such systems have not only to remove a number of different air pollutants simultaneously but have also to regulate humidity and temperature. Among schools these systems are installed in medium to large industrial buildings. However, in some industrial areas, especially in production sites, concentrations of VOCs are found at higher levels and air volumes are much larger. Hence, alternatives to HVAC systems are required for these sites able to fulfill environmental and safety requirements. Some of these VOC mitigation processes are briefly depicted in the next section.
1.2.3. Alternatives methods for waste air purification

Waste air management is a very important task that arises in many industrial processes. Depending to APs that have to be removed and the specific circumstances on sites, the most efficient mitigation method has to be chosen. If we divide air pollutants in their aggregate states, gaseous, liquid (aerosol) and solid, strategies for their individual removal can be deduced. This can be achieved by separation (filtration), washing (absorption) or decomposition (combustion). Separation via filters can be used for solid particulate matter (e.g. dust, soot, pollen) or aerosols. VOCs for instance can be removed via adsorption on the surface area of filters. Depending on the solubility of the APs, air scrubbers may also be used. However, it is clear that such strategies require periodic maintenance and eventually renewal of the purification unit. The decomposition of APs via combustion either in a flame or on a catalyst requires specific conditions (e.g. humidity levels) in order to be efficient. Permanent solutions for VOCs treatment include thermal oxidation, catalytic or photo-catalytic oxidation and aim to decompose VOCs to less harmful products such as CO\textsubscript{2} and water. In the following some of these methods are briefly discussed.

**Thermal oxidation**

Thermal oxidations plants are designed to handle large air flows contaminated with almost all types of VOCs (Figure 1.5). The destruction efficiency can reach more than 95% in a wide concentration range when burning supplemental fuel like propane or natural gas to reach the required temperatures. When operating in air, at temperatures near 1300 K, high levels of nitrogen oxides can be produced as secondary pollutants. Compounds containing chlorine (e.g. pesticide) or nitrogen (e.g. amines) produce hydrochloric gas or additional NO\textsubscript{x}. Hence, the exhaust gas needs further treatment. Additionally, acidic side products may require the use of expensive corrosion resistant construction materials and the use of additional acid gas scrubbing as follow-up treatment [26]. Internal combustion is only suitable for high VOCs concentration since it uses the air pollutant itself as fuel.
Figure 1.5: Schematic view of a thermal oxidizer. Polluted air is flushed into a combustion chamber fueled with propane or natural gas. VOCs are burnt to CO₂ and water. At high temperatures NOₓ may be formed from nitrogen present in air (adapted from [26]).

**Catalytic oxidation**

Catalytic oxidation systems reduce the combustion energy and operate at lower temperatures as thermal oxidizers [27]. The incoming gas stream is heated and passed through a honeycomb or monolithic support, containing the catalyst and reaching destruction efficiencies higher than 90% (Figure 1.6). However, large catalytic systems are not as popular as direct thermal oxidation systems. Even though energy may be saved at lower temperatures, the required catalyst contains often expensive noble metals such as Pd or Pt. Additionally, depending on the catalyst used, the high costs of replacement may also play an important role. Like thermal oxidizers, catalyst systems can produce secondary combustion waste gases. Halogens and sulphur compounds are converted to acidic species and pose the previously mentioned problems. Catalyst materials can be sensitive to poisoning and lose their efficiency [26]. To overcome these problems, a number of catalysts have been investigated. As promising catalyst, V₂O₅-WO₃/TiO₂ has been suggested [28]. This catalyst combines high activity with strong chemical stability towards Cl₂-HCl that may be produced when chlorinated VOCs are oxidized. Additionally, the presence of WO₃ prevents catalyst poisoning by sulfur dioxide, a contaminant often found in waste gases [29].
Figure 1.6: Schematic view of a catalytic oxidation system. Polluted air is pre-heated and passed through a hot catalyst fixed bed. The hot exhaust gas, containing mostly CO₂ and water is cooled in a heat exchange unit. Finally purified air is released at around 300 K (adapted from [26]).

Biological treatment

An additional strategy involves micro-organism. Biological treatments were originally meant for odor abatement of waste gases (Figure 1.7) [30, 31]. This technique is suitable for treating large air volumes with low VOC concentrations (ppm level) [26, 32]. The ability of micro-organisms to convert organic pollutants, under aerobic conditions to water, carbon dioxide and bio-mass is exploited. The bio-filter consists generally of a simple structured packed bed and an immobilized micro-flora. The contaminated gas is directed through a bio-layer around the packing material. A big advantage of this method, is the fact that VOCs are not transferred to another environmental compartment (gas/solid or gas/liquid), but are decomposed on place [26]. The incidental bio-mass can be incinerated or used in down-stream processes.
Figure 1.7: Schematic view a bio filtration system. Polluted air is flushed from the bottom in the reactor containing immobilized micro-organism. The air pollutants are absorbed by the broth where micro-organisms decompose them to CO$_2$, water and sludge (adapted from [32]).

Photocatalytic oxidation

Ultra violet (UV) light is also used for direct decomposition of VOC via radical formation or by using oxidizers such as hydrogen peroxide. One of the most wide spread photocatalysts is TiO$_2$ [33]. This material is suitable for this purpose since the band-gap of 3.2 eV allows activation by UV light from the sun as shown in figure 1.8 [34].

Figure 1.8: Principle of photocatalytic oxidation of VOC on TiO$_2$ (adapted from [34]).
After irradiation, an electron ($e^{-}$) is promoted in a valence band leaving a hole ($h^{+}$) back. At this point, VOCs adsorbed on the surface can be reduced or oxidized. The following reactions happen on the surface:

- **Excitation**: $\text{TiO}_2 + h\nu \rightarrow h^{+} + e^{-}$ (eq. 1.1)
- **Oxidation**: $h^{+} + \text{OH}^{-} \rightarrow \text{OH}^{•}$ (OH$^{•}$ from adsorbed water) (eq. 1.2)
- **Reduction**: $e^{-} + \text{O}_2(\text{ads}) \rightarrow \text{O}_2^{•}(\text{ads})$ (eq. 1.3)
- **VOC oxidation**: $\text{OH}^{•} + \text{VOC} + \text{O}_2 \rightarrow n\text{CO}_2 + m\text{H}_2\text{O}$ (eq. 1.4)

However, as mentioned above, possible harmful side product may be formed in such processes.

**Condensation, absorption and adsorption**

The strategies discussed so far aim to destruct VOCs. However, in some cases especially in industrial processes, recycling of VOCs may be of great value. Recovery of VOCs can be achieved by condensation, absorption and adsorption [35].

Condensation of VOCs happens when the waste gas stream is cooled or pressurized in order to reach an oversaturation. This method is appropriate for high VOCs concentrations and for compounds having boiling points above room temperature. However, the fact that high concentrations are treated, explosive mixtures may be formed in air. Therefore working under an inert atmosphere is preferred [26].

For absorption, the VOCs need to be soluble in a liquid phase. Absorber towers filled with packing material provide the liquid-vapor contact area needed for efficient mass transfer. These systems can reach efficiencies higher than 95% [26]. However, the VOCs removed from the air are just transferred in another phase, which needs further treatments.

VOCs can also be adsorbed. Adsorption is a reversible, physical process driven by weak intermolecular forces (see also section 1.3). The advantage of adsorption consists in the efficient enrichment of VOCs from low concentration waste gases. At high enrichment levels, recovery of VOCs becomes attractive. Regeneration of spent adsorbers, hence, recuperation of captured VOCs, can be achieved thermally or by pressure reduction. Thermal desorption is suitable for compounds with high partial pressure. However, if they are reactive, the VOCs may undergo modifications or even polymerize on the adsorber itself. In this case lowering the pressure will increase the volatility of the adsorbed compounds allowing a much lower desorption temperature [26].
In summary there are several possibilities to control VOCs emissions. Depending on the application, these techniques may be suitable to remove VOCs in an efficient way. However, in domestic areas different circumstances are found compared to an industrial environment. These may include technical aspects, such as lower VOCs concentrations or operational aspects where untrained personnel are more often present. Hence, appropriate techniques are demanded to meet handling, energy and cost requirements. These may consist by small scale combination of methods used in industrial areas as discussed so far. Some materials suitable for this task and their role in VOC control are briefly discussed in the next chapter.
1.3. Activated carbon for air purification

The material found in a pencil consists of ordered graphite sheets. While writing, these sheet glide easily to the paper. When these graphite sheets are randomly oriented, a structure similar to that found in activated carbon (AC) is formed. From about 375’000 tons of AC produced every year, nearly 300’000 tons are used for the treatment of water and other liquids. Only 75’000 tons involve gas-phase applications. AC is mostly used in the USA and Japan whereas only little is consumed in the rest of the world [36]. AC contains over 80 wt. % of carbon and the rest includes oxygen (6 – 7 wt. %), hydrogen, nitrogen, sulfur and ash. Depending on the raw material and production methods, the oxygen content can reach up to 20 wt. % [36]. AC is prepared by pyrolysis of carbonaceous raw martial by, so-called, carbonization below 1073 K under inert atmosphere and is followed by activation in an oxidative atmosphere below 1273 K. Raw materials with high carbon content include charcoal, nutshell, coconut, husk, peat, wood, coir or fossil materials like lignite, coal, and petroleum pitch. The raw materials can strongly affect the properties of the final product regarding e. g. the graphitizing degree [37].

In the first stage (carbonization) most elements like oxygen, hydrogen, nitrogen and sulfur are eliminated. Carbon atoms combine to aromatic sheets and cross-link to each other randomly. These randomly arranged aromatic sheets produce the free space which is richly found in AC. Micro-crystalline structure are found as graphene-like sheets formed during the carbonization process. However, the presence of residual heteroatoms, like oxygen and hydrogen or vacancies in the lattice, disrupts the regularity in the graphene-like sheets. A so-called turbostatic structure is the result [36] (Figure 1.9).

![Figure 1.9](image-url): Ordered tridimensional crystal lattice of graphite (top) and turbostatic structure in activated carbon (bottom) (adapted from [36]).
As mentioned before, AC is a highly porous material. The pore shapes range from ink-bottle like to open or blind capillaries, to regular slits and V-shapes. By definition, pores are subdivided in micro-, meso-, and macropores. Micropores are smaller than 2 nm, mesopores are found between 2 and 50 nm and macropores are above 50 nm (see Figure 1.10) [38].

**Figure 1.10:** Schematic view of the pore structure in activated carbon (dimensions are not in scale).

The adsorption of compounds like VOCs mainly takes place in the micropores as more than 90% of the specific surface area is found there. Adsorption is much stronger in the micropores due to the summation of adsorption forces originating from the adjacent walls which form the pores. Mesopore adsorption is present in a much lower extent, whereas macropores are not considered to be important for adsorption beside the fact that they act as transport channels to meso- and macropores [36]. For low functionalized, crystalline carbon, physical adsorption is the dominant adsorption mechanism. The dispersive London component of the van der Waals interaction is the main driving force in physical adsorption [36]. As the interaction force scales with $1/r^6$, the distance between the molecule to be adsorbed and the carbon surface is very important. Moreover, as London dispersion forces are additive, large molecules tend to interact stronger with the surface than smaller. In principle, every compound that is polarizable can be adsorbed on AC. As a consequence of carbonization and activation, the carbon framework has a diversified chemical structure and corresponding reactivity. Chemical reactivity is mainly localized on the edges of the carbon sheets than on the basal plane. As a consequence, highly graphitized carbon has more basal framework and is less reactive [36]. The edge functionalities are mainly C–O, C–H, C–N, C–S, C–X (X = halogen) groups. Heterocycles are also present. Since the oxygen content is found to be higher than the other elements, C/O containing surface groups are most important as they strongly influence the polarity, the hydrophilicity, acidity and chemical reactivity of the AC [36].
The reaction of AC with oxygen significantly depends on the applied temperature during exposure. Below 673 K, oxygen is chemisorbed and forms C/O functionalities. Above 673 K, surface compounds are decomposed and gasification of carbon takes place (Figure 1.11).

\[
\begin{align*}
\text{C + O}_2 & \xrightarrow{< 673 \text{ K}} \text{C(O)} \\
\text{C + O}_2 & \xrightarrow{< 673 \text{ K}} \text{CO + CO}_2 \\
\text{C(O)} & \xrightarrow{< 673 \text{ K}} \text{CO + CO}_2
\end{align*}
\]

**Figure 1.11:** Temperature dependent oxidation of carbon; stoichiometry is not considered (adapted from [36]).

Depending on the type of oxygen-carbon moieties, AC has acidic, basic or neutral properties. Acidic functionalities can be carboxylic acids or phenolic groups. Basic functionalities are more difficult to determine and are formed in vacuum or inert atmosphere at 1273 K. Neutral functionalities, such as alcohols or epoxides are formed upon chemisorption of oxygen on double bonds within the carbon framework (Figure 1.12).

**Figure 1.12:** Functionalities found in oxidized activated carbon (adapted from [36]).

Investigations regarding removal of organic micro-pollutants from aqueous solutions reveal a disproportional relationship between the sum of N and O found in a carbon, *i.e.* its polarity and the adsorption capacity for an organic pollutant. This is explained assuming a higher water adsorption on polar surface functional groups leading to water clusters that block the access of micro-pollutants to the adsorption sites. Moreover, it was found that micropores which correspond to 1.3 - 1.8 times of the kinetic diameter of the adsorbing molecule, control the adsorption capacity. Hence, the micropore size distribution is an important parameter influencing the effectiveness for adsorption. Depending on the amount of humidity in the air, similar effects may become important for gas phase adsorption of polar VOCs [39]. Other studies conducted with oxidized and non-oxidized AC indicate a stronger affinity for polar
compounds towards the oxidized carbon. Additionally, the oxidation process was found to enlarge the micropores, hence also influencing the micropore size distribution. These results indicate, that oxidation of AC simultaneously influences chemisorption and physisorption of molecules [40]. As explained above, water purification using AC is by far the most popular application of this adsorption material. As a consequence, considerable effort has been put into the modifications of AC for enhancing the adsorptive capacity for specific pollutants. Modifications may include chemical, physical or biological treatment. Chemical modifications are mostly represented by oxidation, increasing the acidity of AC. For instance, this treatment enhances the uptake of metal ions as depicted in figure 1.13 [41].

![Figure 1.13: Suggested cation exchange mechanism involving water as proton acceptor and a metal ion as a ligand to the carboxylic acid (adapted from [41]).](image)

Alkaline treatment increases the uptake of e.g. perchlorate. Biological modifications include a number of micro-organisms adsorbed on AC such as *Pseudomonas putida* which was used for removing phenols from waste water [41].

As mentioned before, pollutants like VOCs can be adsorbed on AC very efficiently. Hence, AC is often used in environmental applications. For instance, in industrial processes, where large solvent quantities are used, a conspicuous portion of the solvents escapes into the gas phase. For cost saving, reduction of environmental impact and respecting emission regulations, recirculation of the used solvent is required. This can be achieved by activated carbon solvent-recovery plants, where contaminated air is passed through a bed of activated carbon. Like this, the solvent is removed by adsorption and clean air is exhausted to the atmosphere. However, moisture can reduce the effectiveness for polar VOC removal, as explained above. Halogenated compounds are more strongly affected by increased humidity as for example aromatic compounds. Since exhaust air contaminated with VOCs is often humid, AC is strongly indicated for high concentration adsorption of VOCs [26]. However, when AC is exhausted, all pores are filled with adsorbate and the material needs to be regenerated. Regeneration of spent AC can be achieved thermally or by other techniques such as pressure swing-desorption.
Regeneration of field spent AC involves drying, thermal desorption under inert atmosphere and residual organic material oxidation by steam or carbon dioxide at high temperature to restore the initial surface area [42]. Under inert or oxidative conditions the adsorbates are pyrolyzed and combusted. Temperatures of about 1000 K are needed and a carbon burn-off between 5 – 15% is usually observed [43]. If regeneration is done on-site using hot air or nitrogen, the removed solvent would simply be released to the atmosphere necessitating further treatment [26]. Regeneration of field spent AC can also be done chemically or following biological methods. Chemical regeneration includes displacement of contaminants by solvents or via wet oxidation techniques. Biological treatments require biodegradable contaminants which are not always present. Alternatives are steam regeneration, in situ catalytic oxidation, microwave desorption, electrochemical ozonation and supercritical solvent extraction. All these methods have advantages and drawbacks. Mostly, they require special facilities to be carried out and are not easily applicable on place [44, 45].
1.4. Zeolites for air purification

The name zeolite comes from the Greek words zeō and lithos which mean “to boil” and “stone”. This name describes the behavior of the mineral like stilbite when it is rapidly heated (Cronsted 1756). In fact, water stored in the material is liberated and large amounts of steam are produced. Zeolites are known for more than 250 years. They are three dimensional alumino-silicate frameworks [46]. As indicated by the name, the open framework consists of silicon (Si), aluminum (Al) and oxygen (O). These elements combine to tetrahedral subunits of [SiO$_4$] and [AlO$_4$] which further connect via common oxygen atoms at the corners to form the regular crystal structure [46]. The empirical formula of such materials can be described as follows:

$$A^{m+}[(\text{SiO}_2)_x \cdot (\text{AlO}_2^-)_y] \cdot z\text{H}_2\text{O}$$

where A is a cation with the charge $m$ the sum of $x$ and $y$ is the tetrahedral number per crystallographic unit cell and the $x/y$ ratio is the silicon to aluminum ratio (Si/Al). Si and Al are referred as T-atoms [46].

![Figure 1.14: Three dimensional structures of selected zeolites](image)

The Al content strongly influences the negative frameworks charge density, the Brønsted acids sites and their strength, the thermal stability and hydrophobicity. As silicon is tetravalent and...
aluminum is trivalent, the net negative charge excess on AlO\(_2^-\) has to be compensated by mono or divalent cations such as sodium (Na\(^+\)) or calcium (Ca\(^{2+}\)). This gives the zeolite the ability to act as an ion exchanger. The acidity of a zeolite is a very important parameter that can be classified according to the nature of the acid sites, their strengths and density within the framework [47]. There are Brønsted and Lewis acids sites. According to the definition, Brønsted acids are proton donors and Lewis acids are electron acceptors. Acidic protons can be generated in zeolites by displacing alkali metals (Na\(^+\)) with ammonium (NH\(_4^+\)) salts. At temperatures between 573 to 673 K, ammonia (NH\(_3\)) is liberated and leaves a proton in the framework [46]. Lewis acid sites are represented by [(AlO\(_2\))]\(^n+\) units originating from the zeolite framework as Al can coordinate lone pairs from e. g. water molecules. This can weaken the O-H bond and generate a proton donor species. As a consequence, the density of Brønsted acid sites is related to the aluminium content of the zeolite [48].

The pores present in zeolites are very narrow and combine to interconnecting channels. These pores can act as a filter allowing only certain species (molecules or ions) to enter the framework. For this reason, zeolites are also called molecular sieves. There are 40 naturally occurring zeolites and more than 150 synthetic zeolites. In synthetic processes the Si/Al molar ratio can be tuned to modify the properties. For instance, high silicon contents will increase hydrophobicity as less negative charge (originating from the presence of trivalent aluminum) has to be compensated. Hence, fewer positively charged ions are present. As a consequence, the acid/base properties of zeolites can also be tuned. For instance, when substituting sodium ions with protons in a cation exchange process. Also, the effective pore size can be slightly modified by substituting a Na\(^+\) ion with a larger K\(^+\) ion [46, 49-51].

Zeolites are valuable adsorption materials for air purification due to their large specific surface area. As humidity may vary significantly in field applications, a robust material able to adsorb VOCs even in humid environments is very valuable. As a result of the good thermal stability and hydrophobicity (large Si/Al ratio), zeolites are increasingly considered as adsorbers. As zeolites are inorganic crystalline materials, they are non-flammable and thermally stable (up to 1123 K). The non-flammable properties of zeolites also allow a save adsorption of highly flammable solvents like hexane. However, as the costs are high, the wide spreading of this versatile adsorber material remains limited especially in domestic areas [26]. However, strongly hydrophobic zeolites are used in so called VOC concentrators as shown in figure 1.15 [52, 53].
Figure 1.15: Schematic representation of a VOC concentrator. In the lower part contaminated air is cleaned by passing the rotor adsorber. VOCs are adsorbed at room temperature. Before saturation is completed, the honeycomb structure containing hydrophobic zeolite rotates towards a region (upper part) where hot air flushes the previously adsorbed contaminant back. The now exhausted air enriched with VOCs can be further treated for instance using a thermal combustion chamber [54].
1.5. Ceria nanoparticles for air purification

As a result of the economic growth mentioned in section 1.2, an increase in transportation is also expected. A conspicuous part of air pollution found in the atmosphere derives from internal combustion engines as found in cars [55]. To overcome this problem, social and political solutions are required that would decrease the need for mobility as experienced so far. Until that happens, technological solutions aiming to reduce pollution are needed. One of these is represented by catalytic converters installed on cars. As a result CO, NOx and particulate matter emissions diminished drastically [55]. Also, a drastic decrease in hydrocarbons emissions such as C4–C8 VOC species was observed as measurements in the Gubristtunnel (Zurch, Switzerland) in 2002 suggest. This is due to the catalytic converter installed in gasoline-fuelled cars [56, 57]. One of the key components in catalytic converters is cerium oxide.

Cerium oxide with the empirical formula CeO₂ contains two equivalents of oxygen and one of the lanthanide cerium. However, if treated in a reducing, oxygen consuming atmosphere, cerium oxide forms nonstoichiometric CeO₂₋ₓ with x being between 0 and 0.5. When heated in a oxidizing, atmosphere CeO₂₋ₓ such as Ce₂O₃ can be transformed back to CeO₂ and regains its oxidative properties.

Figure 1.16: The face centered cubic cell of CeO₂ with the fluorite structure. Atoms are not in scale (adapted from [58]).

Ceria has various applications, ranging from soot removal from diesel engine exhaust to wastewater treatment. It is used as an additive in combustion catalysts and is utilized in electrochemical reactions. Its ductility derives from the ease in undergoing redox transitions leading to a remarkable oxygen storage capacity (OSC). On the surface, this is noticeable as formation and disappearing of oxygen vacancies. When an oxygen atom is removed from the lattice, a so called oxygen defect is the result. The electron left behind reduce Ce⁴⁺ to Ce³⁺ by accommodating the electrons in the Ce 4f state [59]. This can be symbolized by equation 1.5:
The removal of oxygen results in the formation of a Ce$^{3+}$/Ce$^{4+}$ pair. Reduction of ceria can also be achieved by thermal treatment under vacuum (very low $pO_2$) or by applying reducing agents such as H$_2$ as shown in equation 1.6 [60]:

$$2 \text{CeO}_2 + \text{H}_2 \rightarrow \text{Ce}_2\text{O}_3 + \text{H}_2\text{O}$$

(eq. 1.6)

As the formation of oxygen vacancies is facilitated, redox reactions from the type Mars-van Krevelen are likely to happen when using ceria as catalyst [61]. The topmost layer of ceria is composed of oxygen atoms and Ce atoms are situated just underneath. Ceria nanoparticles are dominated by the (111) surface [62]. As these atoms lie at the edge of the crystal, they differ from the fluorite type bulk structure. One side is not coordinated and surface Ce and O atoms have lower coordination numbers. When oxygen vacancies are formed, the electrons transferred to the Ce$^{4+}$ ions form the bigger Ce$^{3+}$ ions and substantial lattice distortion may result. This may additionally influence the ion conductivity of the material. As Ce$^{3+}$ has a larger ionic radius, it has a lower coordination number (CN = 7) than the smaller Ce$^{4+}$ (CN = 8). On the surface of ceria various oxygen species have been recognized such as superoxo (O$_2^-$) and peroxo (O$_2^{2-}$). When oxygen vacancies are repaired by O$_2$, strongly oxidizing peroxo species are formed (eq. 1.7) [60]:

$$[2 \text{Ce}^{3+}, \text{V}_0] + \text{O}_2 \rightarrow [2 \text{Ce}^{4+}, \text{O}_2^{2-}]$$

(eq. 1.7)

However, when subsurface vacancies are healed, only one electron is transferred from Ce$^{3+}$ to O$_2$, resulting in a superoxo species and the formation of mixed oxidative states of Ce is the consequence (eq. 1.8) [60]:

$$[2 \text{Ce}^{3+}, \text{V}_0] + \text{O}_2 \rightarrow [\text{Ce}^{3+}, \text{Ce}^{4+}, \text{O}_2^-]$$

(eq. 1.8)

The surface of ceria can also be characterized in terms of acid-base chemistry. Hydroxyl groups that may be formed upon water chemisorption have a basic character, whereas the Ce$^{4+}$ centre may lead either to Brønsted (chemisorption of H$_2$O) to Lewis type centres [60].

As Ce$^{4+}$ is in a high oxidative state it is considered to be Lewis acidic and O$^{2-}$, with its higher electron density, is the Lewis basic centre. The surface of ceria can be studied by infrared
spectroscopy of adsorbed probe molecules. For probing the surface, molecules which can coordinate to the acid-base centre, are used. Electron donor molecules such as CO or pyridine are used for probing Ce$^{4+}$ centres whereas proton donor molecules such as pyrrole interact with O$^{2-}$ species. From observed dissociative adsorption of pyrrole on O$^{2-}$, a very high basic character of these centres is derived. The adsorption of molecules such as water or methanol increases the coordination of surface cations. Adsorption sites for Lewis acidic molecules such as CO$_2$ are represented by basic OH groups or O$^{2-}$ sites resulting in hydrogen carbonate or carbonate species (see Figure 1.17) [63].

![Figure 1.17: Adsorption of CO$_2$ on Lewis basic centers OH and O$^{2-}$ (top) and anchoring structure on ceria ions (bottom), charges are omitted (adapted from [64]).](image)

As mentioned, adsorption of electron donor molecules occurs on Lewis acidic centres like Ce$^{4+}$ cations in oxidized ceria and with unsaturated coordination sphere. The acidity is weaker on reduced ceria. Adsorption of pyridine, a strong Lewis base, can be used to discriminate Lewis and Brønsted acid sites in IR analyses [65]. Dimethylether, for example, adsorbs on ceria *via* the oxygen lone pairs without dissociation as the acidity of ceria is rather low and is similar to a proton donor [64]. In contrast, the coordination of the oxygen lone pair of water to Ce$^{4+}$ may result in a weakening of the O–H bonds. This weakening may result in a heterolytically split of the bond generating a proton. The proton left is adsorbed on to surface oxygen and forms a hydroxyl species (eq. 1.9).

$$\text{H}_2\text{O} + [2 \text{Ce}^{4+}, \text{O}^{2-}] \rightarrow [2 \text{Ce}^{4+}, \text{O}^{2-}][\text{H}_2\text{O}]^+_a, \text{OH}^-_a;$$  
(eq. 1.9)

Another molecule of interest is NO. This molecule contains an unpaired electron (5 + 6 electrons) and is harmful to humans. Ceria based materials are useful for elimination of this air pollutant. When the O-end of the NO molecules is accommodated in an oxygen vacancy, the
N–O bond weakens and stretches. In case 2 NO molecules adsorb close to each other, the two N atoms combine to form a N₂ molecule which is readily liberated. At the same time, ceria is oxidized [60]. Also alcohols [66] and carboxylic acids can adsorb onto ceria leading to methoxy group formation when methanol is adsorbed and formate species upon formic acid adsorption. Latter is anchored to the surface as showed in figure 1.18 [67]. Decomposition of formate and methoxy groups to form isolated OH and carbonate species occurs at 573 K.

![Diagram of dissociative adsorption of formic acid on ceria](image)

**Figure 1.18:** Dissociative adsorption of formic acid on ceria by forming mono and bidentate formate species (adapted from [67]).

The dissociative adsorption of formic acid may occur *via* dehydroxylation or *via* deprotonation as following:

\[
\text{HCOOH} + \text{Ce}^{4+}\text{O}_2^- \rightarrow \text{HCOO}^-\text{Ce}^{4+} + \text{HO}^- \quad (\text{dehydroxylation})
\]

(eq. 1.10)

\[
\text{HCOOH} + \text{Ce}^{4+}\text{O}_2^- \rightarrow \text{HCOO}^-\text{Ce}^{4+} + \text{HO}_2^- \quad (\text{deprotonation})
\]

(eq. 1.11)

\[
\text{HO}^- + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2^- \quad (\text{eq. 1.12})
\]

**Scheme 1:** Dissociative adsorption of formic acid on ceria dehydroxylation or *via* deprotonation; O₂ indicates a lattice oxygen atom (adapted from [67]).

Methoxy species are oxidized by superficial oxygen in a similar way. As seen, the catalytic properties of ceria originate not only from oxygen vacancies, but also from acid-base pair sites which are also able to activate e. g. hydrocarbons [68]. The oxidative potential of ceria has been showed in various works [58, 69, 70]. It was found that the enhanced oxidative properties of nanostructured ceria is directly related to the Ce³⁺/Ce⁴⁺ ratio and concentration of oxygen vacancies resulting in a higher oxygen storage capacity and as a consequence in a higher oxidative activity [70]. Due to these characteristics, among others, ceria has found broad utilization in catalytic converters for air pollution control in engine exhaust gases as mentioned at the beginning of this chapter.

A catalytic converter has the task to transform or convert harmful pollutants to less harmful products. A possibility is to use a two-way catalyst, where carbon monoxide is oxidized to
carbon dioxide and unburned fuels (hydrocarbons, HC) are eliminated by total oxidation to CO$_2$ and water. As NO$_x$ is not eliminated, a new three-way-catalyst (TWC) was developed in order to fulfil this task. In the TWC, NO$_x$ are reduced to nitrogen by oxidizing hydrocarbons in excess. A TWC consists of a ceramic honeycomb structure coated with γ–Al$_2$O$_3$ which is stabilized by 1–2% La$_2$O$_3$ and/or BaO. The γ–Al$_2$O$_3$ wash-coat is admixed with CeO$_2$ or CeO$_2$/ZrO$_2$ and contains precious metals like Pt or Rh for enhancing catalytic conversion. When fuel is burned in the engine, the combustion is never complete and compounds mentioned above are found in the exhaust gas. These compounds can react on the surface of the catalyst. Pt and Rh are needed for oxidation of CO, HC and reduce NO$_x$. The catalyst runs in two modes: rich and lean. During the rich period, O$_2$ is needed to oxidize CO and HC. This can be achieved by using an oxygen storage component (OSC) like the mentioned high surface CeO$_2$. NO$_x$ can be eliminated by storing as Ba(NO$_3$)$_2$ when reacting with BaO during lean period and converted to N$_2$ during rich, reducing period [71-74]. The following reactions occur in a TWC:

\[
\begin{align*}
\text{Rich: } & \text{CeO}_2 + \text{CO} \rightarrow \text{Ce}_2\text{O}_3 + \text{CO}_2 \quad \text{(reduction of CO to CO}_2) \\
\text{Lean: } & \text{Ce}_2\text{O}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{CeO}_2 \quad \text{(oxidation of ceria)} \\
\text{WGS (over CeO}_2\text{): } & \text{CO or HC} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \\
\text{Reduction NO: } & \text{NO} + \text{Ce}_2\text{O}_3 \rightarrow 2\text{CeO}_2 + \frac{1}{2} \text{N}_2
\end{align*}
\]

(eq. 1.13) (eq. 1.14) (eq. 1.15) (eq. 1.16)

**Scheme 2**: Reaction occurring in a TWC (adapted from [72, 73]).

In summary, ceria plays an important role and is widely utilized in air pollution control processes. However, the excellent oxygen storage capacity properties and the ability to shift from Ce$^{3+}$ to Ce$^{4+}$ forwards CeO$_2$ to a suitable oxidative catalyst without the need for noble metals for certain applications. For instance, mesoporous crystalline ceria nanoparticles were used for the adsorption and catalytic removal of acetaldehyde [75]. These particles were synthesized using block-copolymer templates in modified sol-gel process achieving large surface areas. Another possibility to produce nanoparticles, including ceria based materials, is represented by flame spray pyrolysis. Using this process, several metric tons to 100 metric tons per year can be produced allowing a wide spectrum of application including air purification [76]. Here, metal oxide nanoparticles are produced in a flame by burning precursor salts stabilized in an organic solvent such as 2-ethylhexanoic acid [77]. Here, the high basicity of surface oxygen leads to the chemisorption of 2-ethylhexanoic acid. This observation led to the work presented in the next chapter.
Final remarks

Conclusively, huge effort has been invested by researchers to improve and invent new technologies for air purification. Sadly, it becomes increasingly evident, that huge energy is wasted *e.g.* in institutional or commercial buildings during non-occupied hours and inefficient energy management [78]. New technologies aiming to perform just more efficiently will not alleviate our energy thirst arising from an increased living standard. A cultural change towards a more responsible use of our resources may have a greater impact than the technological progress made in the last fifty years. But we are not yet there. Keeping this in mind, the following studies presented, do not have the ambition to solve all problems associated with the topic. However, they can indeed substantially contribute in the field of sustainable air purification and supply.
2. Regenerable cerium oxide based odor adsorber for indoor air purification from acidic volatile organic compounds

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2.1 Introduction

Reduction of unpleasant odors deriving from volatile organic compounds (VOC) is an urgent need in domestic-, industrial areas and in public transportation. Commonly used strategies for removal of VOC today consist in air exchange, adsorption on activated carbon [79-81] or photo oxidation [33, 82-84]. Unfortunately, all treatments are of considerable energy demand [33, 82], depend on regular and cost-intensive replacement and maintenance, or can produce dangerous side products [15, 85]. When air is simply exchanged, polluted air is usually replaced by fresh air from outside. This procedure requires high volume exchange rates (typically 3 times the room volume each hour). The air then has to be heated up or cooled, and optionally filtered as it often contains particulate matter (e.g. soot/fine dust from car engines or flue gases). Modern air standards require for every ventilation or air conditioning system removal of particulate material [86, 87]. This results in huge energy consumption from air circulation (pressure drop) and cooling or heating (latent heat; 1.2 kJ per m$^3$ and °C temperature difference). More sustainable forms of air purification are needed and should provide alternatives to reduce the massive air exchange and hence heat transfer. Air purifiers usually adsorb unpleasant odors and small particles by simple air circulation through an adsorber unit, typically based on active carbon (adsorption of VOC, smelling compounds) and HEPA (high efficiency particulate air) filters. A significant drawback comes from the necessity to periodically replace adsorber units when their capacity is exhausted [79] since such replacement usually needs working personnel to drive to a site of application and manually install a new unit. Therefore adsorber regeneration on site would help to reduce maintenance intervals and costs. New systems additionally use titanium oxide (TiO$_2$) and UV light to adsorb and remove odor by photo oxidation [33, 82-84]. This prolongs the adsorber’s lifetime. Continuous UV light generation, however, consumes considerable amounts of energy. More recently, nano-confined catalytic oxidation (NCCO, ozone treatment of air in zeolites pores), has emerged as a valuable alternative to conventional air purification systems [88].

Unpleasant odors usually consist of volatile organic molecules from several chemical classes like fatty acids, lactones, aldehydes, ketones, heterocyles, phenols and sulphur containing molecules. Most of these substances are easily adsorbed on activated carbon at ambient temperature and pressure [79-81]. As alternatives to activated carbon for air purification a number of metal oxide nanoparticles, such as MgO, CaO or Al$_2$O$_3$ have been investigated [89]. The removal of halogenated compounds out of air by destructive adsorption on nanoscale oxides has been investigated by Volodin et al. [90]. A well-studied and widely used metal oxide in industrial oxidation catalysis and in air purification is cerium oxide (CeO$_2$)
43

[91]. Its excellent catalytic properties have been reviewed by Trovarelli [58]. More detailed, when CeO$_2$ acts as an oxidizing agent it is reduced to CeO$_{2-x}$ and defects containing Ce$^{3+}$ are formed. It is generally agreed that the main compensating defects in CeO$_{2-x}$ are oxygen vacancies [92]. This non-stoichiometry is possible because cerium is able to change its oxidation state rapidly allowing the reversible addition and removal of oxygen, making CeO$_2$ an oxygen storage material for oxidation reactions. It has been shown for the oxidation of CO that the oxygen atom needed comes from ceria. It is expected that this process involves creation of an oxygen vacancy on ceria leaving a positive charge that is compensated by reduction of cerium [93]. The role of defects enhancing heterogeneous catalytic activity of ceria is accepted but is still an active area of research [94]. Oxygen vacancies defects (OVD) sites have shown to be very important in the oxidation processes e. g. for CO [95, 96]. The enhanced activity can be attributed to the oxygen storage capacity (OSC) of ceria which is linked to the ease of cerium to change oxidation states as mentioned before [94]. We assume that similar aspects play an important role in the oxidation of acidic VOC as described in this work.

Since the 1980s, ceria has been used in three-way-catalyst (TWC) for the abatement of hydrocarbons, carbon monoxide and nitrogen oxides (NO$_x$) out of automotive exhausts [96]. Ceria based catalysts have also been extensively investigated for the removals of volatile organic compounds, optionally after doping with noble metals (e. g. gold) [97] or as mixed metal oxides [98, 99]. Continuous catalytic oxidation, however, would require heating an indoor air volume to about 150 °C, which is unpractical. As current benchmark, air conditioning requires about 10-20 W/m$^3$ (10 K temperature difference) and UV light generation about 0.5-1 W/m$^3$ room, respectively. Here, we propose to combine the beneficial properties of oxidation catalysis (clean conversion of most acidic VOC to CO$_2$ and water) with adsorber systems (no heating/cooling costs) through the use of regenerable adsorbers with oxidative properties. As test compound we used hexanoic acid. This compound is present in exhaled breath in a concentration of 10 ppbv [100]. Additionally, this compound meets the requirements for our study as HA has a penetrant odor. As small acidic compound, it is representative for other small acidic VOC found in human breath or sweat like propanoic acid, butyric acid, isobutyl acid, valeric acid and isovaleric acid [101, 102].
2.2 Experimental

2.2.1 Cerium oxide particle based fixed bed adsorber systems

Cerium oxide (CeO$_2$) (15-30 nm APS, 99.5% purity, 30-50 m$^2$/g SSA) was purchased from Nanostructured & Amorphous Materials Inc. Texas, USA and used as received. Sodium doped cerium oxide (Na/CeO$_2$) was prepared by incipient wetness impregnation: a mixture of CeO$_2$ and sodium carbonate (9.3 wt. % with respect to CeO$_2$; Merck, EMSURE ISO) was produced by adding a 2.5 wt. % solution of Na$_2$CO$_3$ in water to cerium oxide. The humidity of the mixture was adjusted with additional water to produce a granular, homogeneous material. The mixture was let to mature over night at 120 °C in air and was calcined in air at 500 °C for 30 min to yield sodium doped CeO$_2$.

2.2.2 Adsorber material characterization

Both adsorber materials CeO$_2$ and Na/CeO$_2$ were loaded with hexanoic acid (HA, Aldrich, 99%) by first preparing a HA solution in hexane or diethylether, then impregnating the material and drying it under reduced pressure (removal of the solvents) in order to get a final loading of up to 5 wt. % HA on CeO$_2$. Thermogravimetry (TG) analysis (Linseis TG/STA-PT1600) was performed under air (6 L/h) from 20 °C to 600 °C with a heating rate of 10 °C/min. The gas stream from the instrument was analyzed with a mass spectrometry (MS) system (OmniStar™ GSD 320, 60 eV, 1-100 amu, 0.1 s/amu scan time) to identify decomposition products from HA oxidation on the cerium oxide, or desorbed HA itself. The specific surface area (SSA) was determined on a Tristar Micromeritics (Norcross, GA, USA) using the Brunauer-Emmett-Teller (BET) method at 77 K [103]. X-ray diffraction (XRD) patterns were recorded on an X’Pert PRO-MPD diffractometer (Cu-Kα) radiation, X’Celerator linear detector system; PANalytical, Netherlands) with a step size of 0.033 [103]. The particle size distribution of CeO$_2$ was measured using a Lumisizer 6102-83 (12 channels, lambda = 470 nm, 4000 rpm). A stable dispersion was prepared by mixing 1 wt. % CeO$_2$ particles, 0.1 wt. % 2-[2-(methoxyethoxy)ethoxy]acetic acid (TODS, Aldrich, technical grade), in ethanol (technical grade) and zircon oxide (0.2 mm) spheres. A ball mill (Fritsch pulverisette 7, premium line) was used for production of the dispersion that was used for above mentioned particle size distribution analysis. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis was performed on a Tensor 27 (Bruker) spectrometer equipped with a PIKE DiffuseIR accessory. Spectra were collected from 4000 - 400 cm$^{-1}$ (256 scans) using a 10 wt. % KBr mixture.
2.2.3 Adsorber performance tests

Loading of hexanoic acid on the fixed bed was achieved by flushing artificial contaminated air (1.02 m³/day) over the fixed bed adsorber. The contaminated air was prepared by passing compressed air through a gas washing bottle containing liquid HA and equipped with a glass sintered bottom to ensure that all air bubbles had sufficient contact with the HA for saturation. This air stream was then directed on a fixed bed consisting of CeO₂ particles (bed height: 10.5 cm; diameter: 3.5 cm) or Na/CeO₂ particles (4 cm height; same bed mass as for CeO₂, but the sodium doping affords a higher powder packaging density). Potential transportation of entrained HA droplets onto the fixed bed was avoided by inserting glass wool in the upper part of the saturation bottle into the airstream. Use of an upwards mounted tube to transport the HA loaded air further allowed accidentally formed droplets to condense on the walls and flow backwards. Absence of significant droplet entrainment could further be excluded based on the fact that the here experimentally observed HA gas concentrations are in the range of what is thermodynamically expected. The inlet HA concentration was measured at the starting point of the fixed bed before loading (see Figure 2.1) and the outlet concentration was measured after different adsorption times.

![Image](image.jpg)

**Figure 2.1:** Experimental setup to add a representative model compound for sweaty/rancid odors into an indoor air stream consisting of a reservoir containing hexanoic acid (left) and fixed bed (right). Air (1 m³/day) is flushed through the liquid and carries gaseous hexanoic acid to the fixed bed. The transport of aerosols is impeded by a glass wool filter on top of the reservoir.
All sampling was done at room temperature and environmental pressure, and made use of standard air quality testing protocols (2-step procedure: first, the sample is collected on an adsorber tube, then desorbed and analyzed by gas chromatography). Samples were collected using commercial silica gel adsorber tubes (Dräger Typ-G) for acidic VOC and a standardized, calibrated pump (Dräger X-act 5000) using a standard pump rate of 0.5 L/min and sampling times from 15 to 240 min depending on the targeted detection limits. Desorption of the collected hexanoic acid was done by washing the silica gel with 5.0 mL methanol (EMSURE, ISO Reag.) and further analyzing the extract by GC-FID (Agilent GC 6890, average error ± 10%) as directed by the manufacturer. The “used” fixed bed was removed from the saturation setup (Figure 2.1) and transferred into a tubular oven for regeneration tests (Figure 2.2). The adsorber part of the experimental setup is operated in two modes: in the “air cleaner” mode, the acidic organic volatile compounds are adsorbed at room temperature onto the fixed bed (see Figure 2.2). When adsorption was complete (starting breakthrough of HA as detectable qualitatively by smelling or quantitatively using gas chromatography), the fixed bed adsorber was heated up to 220 °C in case of CeO$_2$. During this period, the adsorbed organic volatiles are catalytically oxidized to CO$_2$ and water. Since the system remained open for the whole process, enough oxygen was available to oxidize the contaminant. After cooling to room temperature, the CeO$_2$ fixed bed adsorber was used again for a next “air cleaning” cycle.

![Figure 2.2](image_url)

**Figure 2.2**: Cerium oxide based adsorbers can be operated in two modes: as air cleaners, volatile compounds adsorb from ambient air, the heating is off. During regeneration, the adsorber (open system) is heated up for a short time, resulting in oxidation of the adsorbed compounds, release of carbon dioxide and water, and returning a functional adsorber. The system is then ready for a next (usually multiple hours to days) period of air cleaning.
2.2.4 Preliminary olfactory tests

Preliminary olfactory tests were carried out on CeO$_2$ and Na/CeO$_2$ loaded with 5 wt. % hexanoic acid respectively. Half of the material was heated up to 220 °C for 15 min in a furnace and the other half was kept at ambient temperature. Six volunteers (2 females and 4 males) were selected. All informed volunteers were free of acute respiratory disease like nasal track infections, sinusitis or rhinitis. The test was performed in a well-ventilated room at 22 °C. Samples were located in ceramic vessels with 25 mm in diameter and filled to one third (volume). Study participant were asked to inhale from about 4 cm distance the air above the samples and assign a value from 1 to 6 (1 no intensity, 6 very high intensity) according to their subjective olfactory perception.

2.3 Results and discussion

2.3.1 Catalytic activity

In order to investigate the possibility for clean regeneration, we carried out a number of preliminary experiments on the catalytic combustion of hexanoic acid on cerium oxide using a TG-DTA-MS system. The thermobalance was loaded with different samples of HA on CeO$_2$ or Na/CeO$_2$ nanoparticles and heated up as described in 2.2.2. For HA on CeO$_2$ catalytic combustion was observed between 171 °C and 210 °C with a peak at 191 °C corresponding to the maximum mass change rate and maximum reaction enthalpy. In contrast, doping with sodium delayed the decomposition activity. HA on Na/CeO$_2$ showed a mass loss corresponding to the decomposition of hexanoic acid between 210 °C and 280 °C with a maximum at 263 °C (see Figure 2.3). A second, minor mass change observed between 70 °C and 130 °C derives from the release of water and carbon dioxide probably originating from carbonic acid (chemisorbed CO$_2$, adsorbed water, see mass spectroscopy pattern in Figure 2.4). These results show the ability of CeO$_2$ and Na/CeO$_2$ to decompose hexanoic acid at comparatively low temperatures. In contrast to non-catalytic oxidation, or combustion-assisted VOC decomposition (usually at 600 – 1200 °C), the here used temperatures are amenable for device manufacturing.
Figure 2.3: Thermogravimetric analysis (TG-DTA) of hexanoic acid (C₆-acid) loaded on CeO₂ and sodium-doped cerium oxide (Na/CeO₂). Decomposition occurs at very mild conditions, well below 300 °C, and is characterized by appearance of a rather sharp mass loss. Sodium doping delayed the catalytic oxidation activity of the cerium oxide support by about 70 °C.

Mass spectra recorded during catalytic decomposition runs clearly showed the predominant formation of carbon dioxide and water. Trace amounts of hydrogen (m/z 2) were formed for HA on pure, non-doped CeO₂ compared to HA on Na/CeO₂ and suggests a minor contribution from a cracking type process on the surface of the catalyst. Next to these three main components, traces of a range of lower molecular mass ions were found in the gas stream (from ionization or fragmentation in ion source) suggesting some side product formation during catalytic combustion. From the absence of two main ions (60 and 73 m/z, characteristic for intact hexanoic acid, see Figure 2.4, right) in catalytic oxidation test runs, however, we can conclude that no hexanoic acid desorbed as an intact molecule and escaped the cerium oxide matrix. Note that HA produces a characteristic set of molecule ions when fed into the MS. These peaks are absent in the cerium oxide-catalyzed decomposition samples. The additional m/z found can be attributed to lower molecular mass derivatives of hexanoic acid such as 1-pentene, 2-pentene (cis/trans; both m/z 70), both typical cracking process side products. The observation of traces of hydrogen (s. above) would further be in line with a minor contribution from
cracking. According to MS spectra, different processes are taking place on CeO₂ if compared to sodium-doped adsorbers based on Na/CeO₂. The main differences are visible for hydrogen (m/z 2) and pentene (m/z = 70, stronger on CeO₂). The main oxidation (i.e. formation of water/CO₂) happens in two stages on Na/CeO₂. The first water/CO₂ release is not accompanied by the typical oxidation by-products (see MS traces) and probably originates from the decomposition of carbonates and dehydration. This is not surprising, given the basic properties of sodium (formation of hydrogen carbonates and carbonates) and the hygroscopic nature of the associated sodium species (both sodium hydroxide and carbonates are very hygroscopic). These compounds also form multiple hydrates (e.g. Na₂CO₃ · 10 H₂O) that decompose in this temperature window.

Figure 2.4: Mass spectroscopic analysis of combustion off-gas from thermal decomposition of hexanoic acid (C₆-acid) as vapor (right) and after adsorption on CeO₂ and Na/CeO₂. For HA on CeO₂ formation of cracking by-products such as pentene isomers (m/z = 70) are observed. Sodium doping alters the MS spectra and results in an early water and CO₂ peak associated with hydrates and carbonate decomposition.

These findings are supported by DRIFTS analysis which revealed the presence of carbonates on CeO₂ and Na/CeO₂. Results are summarized in Figure 2.5 and Table 2.1. Major differences from these samples are represented by signals at 1775, 1590, 1448, 1387, 1160 and 881 cm⁻¹ which are less pronounced or absent on untreated ceria. Carbonates found on CeO₂ are likely to arise from chemisorption of carbon dioxide from air [104] whereas carbonates found on Na/CeO₂ are likely to be a combination of chemisorbed CO₂ and residual carbonates originating from treatment with sodium carbonate. In addition, during calcination, sodium oxide is likely to be formed by releasing CO₂ [105] well below decomposition temperature (800 °C [106]). Hence, signals found at 1775, 1448, 1387, 1160 and 881 cm⁻¹ are attributed to sodium
oxide (SDBS database: 1776, 1453, 1378, 1180 and 879 cm\(^{-1}\)). The signal found at 1590 cm\(^{-1}\) may indicate the reduced state of ceria surface for Na/CeO\(_2\) as indicated by Binet et al. [107].

The oxidation peak is very sharp on CeO\(_2\) (lasting about 20 °C, presumably indicating a light-off phenomenon) while it is prolonged on Na/CeO\(_2\) (lasting about 70 °C) as seen in Figure 2.3 and 2.4. In summary, from thermogravimetry analysis the working temperature is estimated to be situated for CeO\(_2\) between 171 °C and 210 °C and for Na/CeO\(_2\) between 210 °C and 280 °C. Average turnover numbers are found to be for CeO\(_2\) TON\(_{171\text{ °C}-210\text{ °C}}\) = 0.96 μmol·g\(^{-1}\)·s\(^{-1}\) and for Na/CeO\(_2\) TON\(_{210\text{ °C}-280\text{ °C}}\) = 0.70 μmol·g\(^{-1}\)·s\(^{-1}\). These values are comparable to values found in the literature [70, 108].
Table 2.1 DRIFTS signal assignment for CeO$_2$ and Na/CeO$_2$

<table>
<thead>
<tr>
<th>CeO$_2$ [cm$^{-1}$]</th>
<th>assignment</th>
<th>Ref.</th>
<th>Na/CeO$_2$ [cm$^{-1}$]</th>
<th>assignment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3690 (3695)</td>
<td>$\nu$(OH), surface adsorbed water</td>
<td>$^{[104, 109, 110]}$</td>
<td>3690 (3695)</td>
<td>$\nu$(OH)</td>
<td>$^{[104, 109, 110]}$</td>
</tr>
<tr>
<td>3437 (3435)</td>
<td>$\nu$(OH), H-bonded water</td>
<td>$^{[109, 111]}$</td>
<td>3437 (3435)</td>
<td>$\nu$(OH), H-bonded water</td>
<td>$^{[109, 111]}$</td>
</tr>
<tr>
<td>1629 (1630, 1628)</td>
<td>surface adsorbed water, carboxylate</td>
<td>$^{[104, 112]}$</td>
<td>1775 (1795)</td>
<td>Na$_2$O, (Na$_2$CO$_3$)</td>
<td>$^{[113]}$</td>
</tr>
<tr>
<td>1548 (1553)</td>
<td>carbonate $^a$</td>
<td>$^{[104]}$</td>
<td>1590 $^b$ (1587)</td>
<td>bi-dentate carbonate</td>
<td>$^{[107]}$</td>
</tr>
<tr>
<td>1383 (1382)</td>
<td>$\nu$(CO$_3$), core carbonate</td>
<td>$^{[109]}$</td>
<td>1448 (1453,1450)</td>
<td>Na$_2$O, Na$_2$CO$_3$</td>
<td>$^{[113]}$</td>
</tr>
<tr>
<td>1328 (1344)</td>
<td>carbonate</td>
<td>$^{[110]}$</td>
<td>1387 (1378, 1396)</td>
<td>Na$_2$O, HCO$_3^-$, $\nu$(CO$_3$) core carbonate</td>
<td>$^{[109, 110]}$</td>
</tr>
<tr>
<td>1060 (1070)</td>
<td>$\nu$_f(OCO), CO$_2^{2-}$</td>
<td>$^{[109]}$</td>
<td>1160 (1180, 1150)</td>
<td>Na$_2$O, $\nu$_f(OCO), CO$_2^{2-}$</td>
<td>$^{[107]}$</td>
</tr>
<tr>
<td>852 (860, 851)</td>
<td>polydentate carbonate, $\pi$(CO$_3$), carbonate $^a$</td>
<td>$^{[104, 107, 109]}$</td>
<td>1060 (1070)</td>
<td>$\nu$_f(OCO), CO$_2^{2-}$</td>
<td>$^{[109]}$</td>
</tr>
<tr>
<td>723 (730)</td>
<td>$\nu$(CeO) fundamental</td>
<td>$^{[109]}$</td>
<td>881 (854 (860, 851))</td>
<td>Na$_2$CO$_3$</td>
<td>$^{[113]}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>723 (730)</td>
<td>polydentate carbonate, $\pi$(CO$_3$), carbonate $^a$</td>
<td>$^{[104, 107]}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\nu$(CeO) fundamental</td>
<td>$^{[109]}$</td>
</tr>
</tbody>
</table>

$^()$ Wavenumber in parenthesis are values found in literature
$^a$ chemisorbed CO$_2$ from air $^{[104]}$
$^b$ reduced state of ceria surface $^{[107]}$

2.3.2 Regenerable CeO$_2$-based adsorber performance

The outlet concentration of hexanoic acid after passage over the cerium oxide based fixed bed confirmed a high affinity of the adsorber material for the volatile, HA (Figure 2.6, Table 2.2). The off-gas remained nearly odorless for a prolonged time (adsorber fully working) and then subsequently allowed HA to slip through. For cerium oxide, the experiment was carried out using three different inlet concentrations. From data collected it can be seen that for about 50 h no hexanoic acid (below limit of detection, LOD) breaks through the CeO$_2$ bed when using an inlet concentration of about 0.044 mg/L (clearly identified as “strongly smelling” by humans) and a gas hourly space velocity (GHSV) of 440 h$^{-1}$. After that, a maximum outlet concentration (break through) is measured at about 70 h followed by a slight decrease in concentration up to 170 h after starting the adsorption process (see Figure 2.6). The minor decrease in concentration after breakthrough of HA may be a result of starting autoxidation of the hexanoic acid in the reservoir, or through bed restructuring. A second test run used a
hexanoic acid inlet concentration of 0.028 mg/L and samples were taken up to 240 h after start (a longer experiment at lower inlet concentration than in the first experiment). A maximum outlet concentration of 0.015 mg/L was measured after 90 h. After about 10 days, the HA concentration in the outlet had dropped to about 0.011 mg/L. The fixed bed of this second run was regenerated (oxidation of the HA as described in 2.2.3) and reused as adsorber. In a third run, an initial HA concentration of 0.035 mg/L was applied. After 70 h, again no HA could be detected in the outlet gas stream. After 157 h a concentration of 0.018 mg/L HA was measured indicating breakthrough of the test compound (Figure 2.6, green squares). This shows the ability of CeO$_2$ to adsorb HA out of air and to be regenerated without noticeable loss in performance.

**Figure 2.6**: Adsorption of hexanoic acid at relevant indoor concentrations on CeO$_2$ based fixed beds. Bed saturation and breakthrough occurred between 53 and 65 h (1$^{st}$, 1.02 m$^3$/d, $C_{inlet} = 0.044$ mg/L) and between 64 and 90 h (2$^{nd}$, 1.02 m$^3$/d, $C_{inlet} = 0.028$ mg/L). A regenerated fixed bed (2$^{nd}$ regenerated, 1.02 m$^3$/d, $C_{inlet} = 0.035$ mg/L) again showed no breakthrough up to 70 h and confirmed that regeneration was possible without significant loss of adsorption capacity (average error ± 10%).

Sodium doped adsorber Na/CeO$_2$ was used in a first experiment with a fixed bed height equal to that of pure CeO$_2$. Due to its higher packaging density, though, about 2.7 times more material was needed to fill the fixed bed volume. This set up was so efficient, that even after 170 h (1 week) no hexanoic acid was detected in outlet gas stream at an inlet gas HA concentration of 0.056 mg/L and a gas hourly space velocity (GHSV) of 440 h$^{-1}$ (see Figure 2.7). A second experiment with the same mass of adsorber material as the pure cerium oxide was designed (10.0 g adsorber per bed) and resulted in a 4 cm high bed and GHSV of 1100 h$^{-1}$. Here, for up to 96 h, no breakthrough of the HA was observed suggesting a higher capacity for Na/CeO$_2$ in adsorbing hexanoic acid than CeO$_2$, in line with an expected contribution of the alkaline sodium to fix HA as a carboxylic acid salt.
The efficiency of an adsorber can be calculated by following formula:

\[ A_{\text{eff}} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \]

where \( C_{\text{in}} \) and \( C_{\text{out}} \) are the inlet and outlet concentrations of hexanoic acid in the gas stream.

Where no hexanoic acid was found, the limit of detection (LOD) of the here used chromatography and adsorption based standard analysis method was used. Results are summarized in Table 2.2. For CeO\(_2\) we measured an about 2 wt. % mass increase after breakthrough which corresponds to a surface coverage of about 2.5 \( \mu \)mol/m\(^2\). The mass gain for Na/CeO\(_2\) is a combination of hexanoic acid, humidity and carbon dioxide.

### Table 2.2 Adsorber efficiency of cerium oxide based materials

<table>
<thead>
<tr>
<th>Adsorber Material [g]</th>
<th>1(^{st}) CeO(_2) Batch</th>
<th>2(^{nd}) CeO(_2) Batch</th>
<th>2(^{nd}) CeO(_2) Batch Regenerated</th>
<th>1(^{st}) Na/CeO(_2) Batch</th>
<th>2(^{nd}) Na/CeO(_2) Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{\text{in}}) HA [mg/L]</td>
<td>0.044</td>
<td>0.029</td>
<td>0.035</td>
<td>0.056</td>
<td>0.056</td>
</tr>
<tr>
<td>Time, no detection [h]</td>
<td>(\geq 53)</td>
<td>(\geq 64)</td>
<td>(\geq 70)</td>
<td>(\geq 170)</td>
<td>(\geq 96)</td>
</tr>
<tr>
<td>Max. (A_{\text{eff}}) [%] (^a)</td>
<td>96.5</td>
<td>94.6</td>
<td>95.6</td>
<td>97</td>
<td>97</td>
</tr>
</tbody>
</table>

\(^a\) Max. \(A_{\text{eff}}\) [%] is related to the inlet concentration of HA in the single experiment and refers to the time where no HA has been detected. The limit of detection (LOD) for this method is 1.6 \( \mu \)g/L air (average error \( \pm 20\% \)) and \(A_{\text{eff}}\) [%] gives the minimum value for efficiency related to \( C_{\text{in}} \) and LOD. However, where no HA was detected this value might be higher. \(^b\) Fixed bed height was 10.5 cm, \(^c\) fixed bed height was 4 cm

#### 2.3.3 Preliminary olfactory tests by volunteers

Preliminary human olfactory tests showed that the overall perception of smell over adsorber materials with equal loads of hexanoic acid was stronger on CeO\(_2\) than on Na/CeO\(_2\) (see Figure 2.8). This can be explained by a lower partial pressure of hexanoic acid over the carrier material resulting from a stronger binding on the surface. Addition of sodium carbonate as doping agent results in an increased number of adsorption, preferably alkaline centers located on the carrier material. The ability to deprotonate the carboxylic acid of the test compound yields a salt of very low volatility. The formation of the salt species is supported by the observation of an early CO\(_2\) and water release peak in the mass spectrometry analysis (Figure
2.4) and the shift of decomposition/oxidation of the HA at higher temperature. After temperature treatment both carrier materials had lost their capability to emit “bad smell”.

**Figure 2.7:** Sodium doped cerium oxide is an efficient adsorber for hexanoic acid. Up to 170 h (1st run; height of the fixed bed kept constant at 10.5 cm, gas flow of 1.02 m³/d, \( C_{\text{inlet}} = 0.056 \text{ mg/L} \)) and to 96 h (2nd run; mass of adsorber kept constant at 10 gram per bed, gas flow of 1.02 m³/d, \( C_{\text{inlet}} = 0.056 \text{ mg/L} \)) no breakthrough of hexanoic acid was observed (average error ± 10%).

**Figure 2.8:** Preliminary human olfactory tests on CeO₂ and Na/CeO₂ loaded with 5 wt. % hexanoic acid before and after temperature treatment at 220 °C. A rating of 6 corresponds to a (subjectively rated and perceived) level of very intense smell whereas 1 was rated as “no smell at all”.
2.3.4 Adsorber material characterization

BET analysis showed an increase in particle diameter and a decrease in specific surface area (SSA) when CeO$_2$ was doped with sodium. After loading the carrier material with HA and heating up to 600 °C both materials showed some decrease in SSA (see Table 2.3). This effect was much more pronounced for sodium doped cerium oxide. In this case sodium acts as melting point lowering agent. Since preparation of Na/CeO$_2$ involves calcination for 30 min at 500 °C, some particle growth was observed. Even more pronounced sintering was observed for treatment at 600 °C whereas little particle growth was found for pure CeO$_2$. A similar behavior has been observed by Zotin et al. in temperature programmed reduction of sodium doped ceria [114].

The primary particle diameters were calculated from the SSA according to following formula:

\[
D = \frac{6}{SSA \cdot \rho}
\]

where \(D\) is the primary particle diameter, SSA is the specific surface area and \(\rho\) is the density of the material. X-ray diffraction and TEM micrographs (see Figure 2.9 and 2.10) confirmed these SSA derived particle size range.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}} [\text{m}^2/\text{g}])</th>
<th>(D_{\text{BET}} [\text{nm}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$ as prepared</td>
<td>70.4 to ± 3.5</td>
<td>12</td>
</tr>
<tr>
<td>Na/CeO$_2$ as prepared</td>
<td>44 ± 2.2</td>
<td>19</td>
</tr>
<tr>
<td>HA on CeO$_2$ / 600°C</td>
<td>61.6 ± 3.1</td>
<td>13</td>
</tr>
<tr>
<td>HA on Na/CeO$_2$ / 600°C</td>
<td>21 ± 1</td>
<td>38</td>
</tr>
</tbody>
</table>
Figure 2.9: X-ray diffraction (XRD) confirmed an increase in crystallite size (calculated by Debey-Scherrer equation) of CeO$_2$ treated with sodium carbonate and heated up to 600 °C for 1 h if compared to untreated CeO$_2$. Removal of adsorbed HA from CeO$_2$ at 600 °C and regeneration of the fixed bed adsorber showed a negligible degree of sintering, in agreement with nitrogen adsorption measurements (BET).

Figure 2.10: The particle size distribution as measured in a liquid dispersion and electron micrograph (top left) of CeO$_2$ as received. 84% of the particles had a hydrodynamic diameter of 59 nm or less with a median situated at 38 nm (blue line: log-normal particle size distribution calculated). Transmission electron micrographs of Na/CeO$_2$ as prepared (top right) and after heating up to 600 °C in air (bottom right) which affords considerable particle growth due to sintering.
2.4 Conclusion

In a model experiment nano-particulate CeO$_2$ and CeO$_2$ doped with sodium were tested as adsorber material for the removal of bad smelling volatile compounds out of ambient air. Hexanoic acid (HA) was used as test compound. The catalytic activity, for total oxidation of HA after adsorption, was tested in a TG/DTA for CeO$_2$ and Na/CeO$_2$. In air, quantitative combustion was observed on CeO$_2$ between 171 and 210 °C reaching a peak at 191 °C. On Na/CeO$_2$ combustion was delayed to higher temperatures at 210 to 280 °C with a peak at 263 °C. From mass spectrometry analysis no desorption of HA was observed. When passing the model indoor air over the adsorber as a fixed bed, cerium oxide could retain ≥ 96.5% hexanoic acid over a period of 60 h (C$_{in}$ = 0.044 mg/L) and sodium doped cerium oxide reached an efficiency of ≥ 97% for over 90 h (C$_{in}$ = 0.056 mg/L). Taking into account the different space velocities, namely 440 h$^{-1}$ for CeO$_2$ and 1100 h$^{-1}$ for Na/CeO$_2$ a more effective adsorption capacity can be deduced for sodium doped ceria. A full regeneration of the CeO$_2$ was then performed at 220 °C in air. This material could be reused as adsorber without loss in efficiency. The specific surface area determined for CeO$_2$ showed a minor decrease from 70 to 62 ± m$^2$/g upon heating up to 600 °C for 1h in air. This minor sintering was confirmed by X-ray diffraction analysis and transmission electron micrographs. The origins of catalytic activity of CeO$_2$ have been discussed in section 2.1. A possible decrease in activity may arise from (a) loss in surface area or (b) loss of active sites. Surface area loss, as shown in Table 2.3, was small for CeO$_2$ upon heating to 600 °C. From this data it can be assumed that regeneration of CeO$_2$ in a temperature range below 300 °C will not significantly reduce surface area of CeO$_2$ needed for adsorption and catalytic oxidation. On contrary, the Na supplement has shown to significantly decrease surface area as measured by BET after calcination at 500 °C. A similar behavior has been observed by Zotin et al. in the temperature programmed reduction of sodium doped ceria where BET surface area decreased from 120 m$^2$/g to 70 m$^2$/g after treatment at 400 °C [114]. The stability range of sodium supplemented CeO$_2$ has not yet been completely investigated.

Deactivation may also comprehend loss of oxygen vacancies defects (OVD) and oxygen storage capacity (OSC). Additionally, the supply of oxygen originating from CeO$_2$ must be ensured. As regeneration happens in an open system well above room temperature, reoxidation of ceria can be assumed to happen during this process. This will restore the initial conditions needed for the next cycle [109, 115]. Addition of sodium is expected to generate basic center on the CeO$_2$ particles. There, the carboxylic acid may be more easily deprotonated and fixed more efficiently on the adsorber. This hypothesis was indeed confirmed as shown by an
increased capacity of the adsorber material to capture HA (see TG experiments and a delayed breakthrough of HA in Na-doped ceria (Figure 2.7)). The here shown two step batch treatment is more energy efficient compared to continuous oxidation of contaminated air. Since the catalytic combustion of hexanoic acid peaks at around 190 °C, the continuous oxidation would require heating the catalyst at least to that temperature for the whole air cleaning period. Additionally, the contaminant concentration is expected to be low during that period. Batch treatment, however, removes contaminants at room temperature after first enriching them on the catalyst until a regeneration cycle is required. This lasts for only a fraction of the time compared to continuous oxidation mode which is much more energy efficient. In summary, CeO$_2$ showed very promising properties for application as an air cleaner due to its very good ability for adsorbing the representative model compound hexanoic acid out of contaminated air and for its capability for recycling at comparatively low temperature. Na/CeO$_2$ adsorbed hexanoic acid even stronger than CeO$_2$ alone but required a higher activation temperature for total oxidation of the test compound. This work shows the ability of cerium oxide to act as an “on place” regenerable air cleaner adsorber material and hence to substantially reduce energy consumption deriving from conventional air purification systems and room ventilation.
3. Physical mixtures of CeO$_2$ and zeolites as regenerable indoor air purifier: Adsorption and temperature dependent oxidation of VOC

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3.1 Introduction

Ensuring good indoor air quality at low maintenance costs is a major challenge in highly frequented buildings such as hospitals, schools, commercial- and industrial areas. Presently used heating, ventilation and air condition (HVAC) systems in building, suffer from high costs rising from unit replacement, in particularly from exhausted adsorbers [79] and huge heating or cooling cost of the exchanged air. The regeneration of indoor air is a particularly valuable alternative in industrial processing, where polluted air simply cannot be fed in the environment. Other techniques studied for air purification include activated carbon [79-81] or photo catalytic oxidation [33, 83, 84]. From an energy consumption standpoint, it would be most attractive to exchange as little air as possible, and maintain adsorber units over a long time without service intervals. We have recently addressed the possibility to regenerate adsorbers using hexanoic acid as a model test compound for acidic volatile organic compounds (VOC) [116], a model for sweat odor. The collected air pollutant was oxidized on a cerium oxide fixed bed. Unfortunately, most odor contaminations in air contain a much broader variety of compounds, often of limited chemical reactivity and include numerous alkenes and even organic bases. A two-step approach is particularly attractive in terms of energy used [116] since contaminated air is not heated/cooled during odor/contaminant removal: energy-intense heating is only applied during regeneration of the adsorber (see Scheme 3.1). In contrast to classical adsorbers (e. g. activated carbon), no system parts require cost and material-intense replacement.

Scheme 3.1: A two-step air cleaning system. At room temperature, VOC are adsorbed on a bi-functional fixed bed. During regeneration, the adsorber bed is briefly heated up and catalytically oxidizes the collected contaminant.

In this work we therefore investigated the possibility to extend this energetically attractive 2-step process to more challenging, representative compounds found indoors. Unfortunately, pure CeO$_2$ as recently used [116] poorly adsorbs most hydrocarbons and common VOC. To overcome this problem we therefore followed the idea of combining classical adsorber materials, such as zeolites, with oxidative catalysts as an intimate physical mixture. In the
present study we demonstrate that mixing CeO$_2$ particles at the 50 to 100 nm scale and classical VOC adsorbers indeed permits energy efficient air purification. More specifically, the here-used material include CeO$_2$ as an oxidative catalyst, and two broadly used zeolites, H-ZSM-5 and 13X for intermediate VOC storage. In the following, important adsorption and catalytic properties of these materials are discussed in order to better understand the here presented results.

The influence of chemical structure of VOC on conditions required for total oxidation has been addressed by O’Malley and Hodnett [117]. They investigated the reactivity of molecules with different functional groups (e.g. alcohols, ketones, carboxylic acids, aromatics and alkanes) over platinum catalyst supported on β-zeolite, mordenite, silica or alumina. The observed reactivity pattern was alcohols > aromatics > ketones > carboxylic acids > alkanes. A correlation was found between the reactivity of the single substrates and the strength of the weakest C-H bond in the molecule. A single weak C-H bond in the molecule indicates a higher reactivity. After its rupture further oxidation steps often involve free radicals.

Pure cerium oxide, a classical oxidation catalyst, can adsorb organic molecules in different ways: electron deficient cerium ions (Lewis acid sites) on the surface coordinate lone pairs of oxygen or nitrogen in organic molecules (e.g. dimethylether). On contrary, electron rich centers such as O$_2^-$ can act as Lewis bases and deprotonate hydroxyls moieties (e.g. alcohols or carboxylic acids) [64]. The zeolite H-ZSM-5 (PZ2/100H) has pore dimensions of 5.1 x 5.5 Å and is the acidic form of an alumo-silicate zeolite with a SiO$_2$/Al$_2$O$_3$ molar ratio of 100:1. Its high silicon content in the acidic (H$^+$-form) rather than the basic form (Na$^+$-form) make this zeolite hydrophobic. Prins et al. [118] have investigated the sorption of VOCs (i.e. methanol, methyl ethyl ketone, toluene, p-xylene and n-pentane) on hydrophobic zeolites at room temperature and found them to break through in the same order as their partial pressure. An extended survey about acidity in zeolites can be found in the literature [48-51]. The so called zeolite 13X (Faujasite X or NaX) is larger, and has a pore diameter of about 10 Å. Díaz et al. [119] have characterized the adsorption of VOCs (alkanes, cyclic and aromatic hydrocarbons and chlorinated compounds) on alumina, zeolite 13X, 5A and activated carbon. While adsorption enthalpy increased with molecular size, a stronger interaction was found for increasing solute polarity. Xie et al. [120] found that diffusion in zeolites is strongly related to adsorption strength on the accessible surface. The influence of the form (parent or protonated) of different zeolites towards reactivity (catalytic oxidation of n-hexane and benzene) has been studied by Díaz et al. [121] They found that reactivity correlates with surface acidity, morphological parameters and adsorption properties. Generally, the protonated form of a given
zeolite results in an increased adsorption strength. An Eley-Rideal mechanism for catalytic combustion of these compounds has been suggested, where a hydrocarbon molecule is first adsorbed and then reacts with gas phase oxygen. This leads to faster overall reaction when adsorption is stronger [121]. The effect of pore structure of zeolites (13X among others) on VOC adsorption has been investigated by Kim et al. [122].

The aims of this study were to increase the understanding for adsorption and combustion behaviors of different VOC classes on zeolite/ceria physical mixtures. As a consequence we wanted to show that the concept of combining VOC adsorber and oxidative catalyst, can be a valuable and efficient alternative to conventional single use adsorber as the here presented adsorber material can be regenerated on place.

3.2 Experimental

3.2.1 Carrier material preparation

Cerium oxide (CeO$_2$) (15-30 nm APS, 99.5% purity, 30-50 m$^2$/g specific surface area, SSA) was purchased from Nanostructured & Amorphous Materials Inc. Texas, USA and used as received. H-ZSM-5 was purchased from ZEOCHEM, Uetikon, Switzerland (PZ-2/100H, 3 μm) and 13X from Sigma-Aldrich (3-5 μm powder). Cerium oxide/H-ZSM-5 calc. was prepared by intense mechanical mixing of CeO$_2$ and zeolite H-ZSM-5 in a 50 wt. % mixture. The mixtures were milled (Fritsch Pulverisette 7, premium line, 0.1 mm ZrO$_2$ spheres, 2 x 20 min 1100 rpm, 30 min break) in water to get fine dispersions. After drying, the fine powder was calcined (calc.) at 500 °C for 1 h in air. H-ZSM-5 calc., CeO$_2$/13X calc. and 13X calc. were prepared in the same way as the cerium oxide/H-ZSM-5 calc. To minimize pressure drop over the fixed bed in breakthrough experiments, the adsorber material powder (except for CeO$_2$) was compressed to granules with a hydraulic pellet press (Specac Ltd., 5t, 30s) and crushed with a mortar. The sieve fraction from 200-400 μm (Filtra vibración S. L. AISI 304 stainless steel) was selected for further experiments.
3.2.2 Adsorber material characterization

All five adsorber materials (pure components and mixtures) were wet loaded with test compounds through soaking the material in diethylether based dilute solutions containing the following compounds: (±)-Linalool (Fluka, purum), triethylamine (TEA, Aldrich, 99.5%), S-(−)-limonene (Fluka, 99% GC) and hexanoic acid (HA, Aldrich, 99%). All model compounds were first dissolved separately in diethylether (Sigma-Aldrich, ≥ 98.5% GC). Wet impregnation of the material was achieved by drying the pre-soaked adsorber granulates in air (removal of the solvents and part of non-adsorbed solute), similar to the routine catalyst preparation method called “incipient wetness impregnation”. A final loading of up to 5 wt. % organic substance was chosen. As a control experiment pure diethylether was added to the adsorber materials in order to distinguish effects raising either from the solvent or from the above mentioned model VOC compounds. In a second series of experiments, gas phase adsorption of linalool, limonene and TEA vapor was tested. The adsorber material was exposed during 24 h to a saturated VOC atmosphere in a closed plastic tube (Techno Plastic Product AG, TPP, 50 mL), which contained a small glass bottle (Fialax, 5 mL) with the corresponding adsorber material and, outside the glass bottle, 2 mL of the corresponding compound. After exposure, samples were ventilated at room temperature for about 30 min and subsequently analyzed by thermogravimetric analysis (TG, Linseis TG/STA-PT1600) under air (6 L/h) from 20 to 400 °C (heating rate of 10 °C/min). The gas stream from the instrument was directly analyzed with a mass spectrometry (MS) system (OmniStar™ GSD 320, 60 eV, 1-100 amu, 0.1 s/amu scan time) to identify decomposition products. The specific surface area (SSA) was determined on a Tristar Micromeritics (Norcross, GA, USA) with nitrogen at 77 K. Samples were desiccated for 4 h at 300 °C before measurement. Micrographs were taken with a HD2700CS (Hitachi, aberration-corrected dedicated STEM, operated at 200 kV) with EDX spectrometer (EDAX) and scanning electron microscope (FEI NovaNanoSEM 450) operated at 30 kV with STEM and EDX detector. Samples were placed on a copper/carbon grid.

3.2.3 Adsorber performance tests

Selected adsorber material samples (1 g) were filled in a glass column (length = 7 cm, i. d. = 1 cm) with glass wool at the bottom. Compressed air was flushed through a glass sintered filter in a gas washing bottle at a flow rate of 250 mL/min in presence of the VOC triethylamine (TEA) as a test compound (see Scheme 3.2). The gas concentration was measured before and
after the fixed bed during adsorption progress. TEA air samples were analyzed by gas-chromatography for high TEA concentrations. Air samples were collected on a sampling tube (Dräger, Type ADS) using a calibrated pump (X-act 5000). The adsorber material was then washed with methanolic potassium hydroxide and analyzed with a GC-FID system (Agilent 6890) using di-isopropyl amine as an internal standard. Low TEA concentrations were determined by using a direct method where air was passed on a Dräger tube (Triethylamine 5/a, 60 ppm) via a manual pump (Accuro Dräger). The color changes on the tube allowed the determination of TEA concentration in air. Specific adsorber batches consisting of CeO\textsubscript{2}/13X (20/80 wt. % calcined at 400 °C for 1 h in air) were regenerated after breakthrough by heating the column containing the fixed bed in an oven (Nabertherm furnace) at 400 °C for 30 min in air. The air purification and regeneration cycle (TEA loading) was repeated three times.

Scheme 3.2: Adsorption of triethylamine (TEA) on fixed beds. A defined air flow is passed through a TEA reservoir (cooled to –30 °C to control the partial pressure) transporting contaminated model indoor air to the fixed bed for adsorption. In sampling port 1, the inlet concentration of TEA is collected on a sampling tube while in sampling port 2, the outlet concentration, after passing through the adsorbed material was directly determined by a colorimetric reaction (see experimental section).

### 3.3 Results and Discussion

The adsorption of diethylether, TEA, limonene, linalool and HA on single components (CeO\textsubscript{2}, 13X calc., H-ZSM-5 calc.) and physical mixtures (CeO\textsubscript{2}/13X and CeO\textsubscript{2}/H-ZSM-5, see Fig. 3.1) were first studied after wet impregnation at room temperature. As a measure of the adsorption affinity of the solute on the support, the corrected mass loss (rel. Δm\textsubscript{400°C} in %, see eq. 3.1 and 3.2) was used (see ESI SA1 and SA9):
where \( \Delta m_{400°C}(\text{Compound}) \) and \( \Delta m_{400°C}(\text{Compound + Diethylether}) \) are the mass loss at 400 °C of wet impregnated supports and \( \Delta m_{400°C}(\text{Blank}) \) corresponds to non-impregnated support. As an indicator for catalytic activity, \textit{i.e.} oxidative decomposition of adsorbed molecules, the exothermic peak maximum (\( T_{\text{exo}} \)) in TG analysis was used (see ESI SA2 and SA9). In some cases, more than one exothermic event was observed. The data were usually listed in the order of increasing boiling point to improve readability.

3.3.1 Adsorption of single components on adsorbers

\textit{One compound systems}

The amount of VOC adsorbed on CeO\(_2\) roughly correlates with the boiling point of these compounds (see ESI SA1). Diethylether, as a weak polar compound, can coordinate with the lone pair of the oxygen atom to ceria cations on the surface. This interaction is very weak since the two ethyl residues shield the oxygen atom when rotating fast at room temperature. Hence, only weak interaction is expected with ceria. The very high partial pressure at room temperature (see Table 3.1) also shifts the equilibrium to the gas phase. This observation is in agreement with a study by Binet \textit{et al.} [64] For triethylamine (TEA) a similar explanation can be used. Even though TEA is a strong Lewis base and the lone pair of nitrogen might coordinate to ceria cations on the surface, the three ethyl residues well shield the lone pair. Hence, only a weak interaction is observed. However, acidic hydroxyl residues (originating from adsorbed water) might be deprotonated, forming triethyl ammonium/Ce-O-pairs. The monoterpene limonene is sensitive to light, heat, base, acid and is easily oxidized to carvon. Possible reactions involving oxygen and carbon dioxide may form polylimonene carbonate [123-125]. Such conditions are indeed given during adsorption and TG-DTA experiments. Even though no strong interactions with the surface are expected as limonene is largely non-polar, the formation of oxidized species enhances the mass gain by immobilization of limonene on ceria. The olfactory compound linalool contains a tertiary alcohol (pKs ~ 17, see Table 3.1) which might be deprotonated by \( O^2- \) species on the surface of ceria [64]. This dissociative adsorption could explain the higher
mass gain (2.4%) if compared to limonene (1.5%) in spite of a similar boiling point of the pure compounds. The carboxylic acid hexanoic acid is easily deprotonated (pKs ~ 4.9, see Table 3.1) on the surface, forming carboxylate species. As such it is expected to have the strongest interaction among the selected VOC.

![Figure 3.1: Energy dispersive X-ray spectroscopy (EDX) mapping of 50/50 wt. % CeO$_2$/H-ZSM-5 (purple/blue = Ce, green = Si, yellow = Al). EDX mapping of the other physical mixtures and pure CeO$_2$ and 13X can be found in supporting information (ESI). Element mapping confirmed physical mixing at a 100 nanometer scale.](image)

The small pore, acidic zeolite H-ZSM-5 (PZ2/100H) adsorbs significant parts of diethylether. All other compounds were poorly adsorbed. Even though kinetic diameters differ depending on the used calculation method, diethylether is the smallest molecule of all here investigated VOC and best fits into the small pores (see Table 3.1). The other compounds (e. g. TEA) are larger and may only interact with outer surface silanol groups [126]. Since all VOC were dissolved in diethylether during wet impregnation, a competition between the solvent and the compounds even favors adsorption of diethylether. In contrast, gas phase adsorption of pure limonene (Fig. 3.2 and 3.3 and see ESI Table SA3) showed a very strong limonene mass deposition on the zeolite (compare section 3.3.3): after several hours of exposure, H-ZSM-5 samples turned pink as a result of above mentioned oxidative polymerization already at room temperature. In line with this interpretation, the pink colored H-ZSM-5 samples turned grey after TG-DTA experiments up to 400 °C, presumably due to carbon deposits as a result of decomposition.

As 13X has a pore diameter of about 10 Å, no mechanical sites discrimination (depending on kinetic diameter) were expected. However, a remarkably low mass uptake was observed for most VOC (see SA1). It is known from literature that adsorption correlates with molecular size and polarity [119]. Additionally, moisture negatively affects the uptake of hydrophobic rather than hydrophilic compounds [127]. This may explain the larger mass uptake of HA if compared to limonene and linalool (see ESI SA1). The practically inexistent adsorption of TEA in wet impregnation (within the margins of error) might be related to its high volatility. It is important
to remember, that all impregnation solution of VOC were dissolved in diethylether. Hence, adsorption of diethylether is favored by its high concentration.

**Mixed CeO$_2$/zeolite systems**

The mass gain of TEA and limonene on mixed material CeO$_2$/H-ZSM-5 is different than what would be expected from the mixture’s content of single constituents (see ESI SA9). The here used intense milling in water together with H-ZSM-5, followed by calcination at 500 °C for 1 h in air might have significantly altered the available surface sites. As limonene can easily be oxidized (a process presumably supported by ceria), an intermediate reaction product might interact stronger with H-ZSM-5 or CeO$_2$ resulting in the here observed, increased mass deposition if compared to the pure constituents. Linalool and hexanoic acid deposition was intermediate if compared to pure zeolite and CeO$_2$ (see ESI SA9). The strongly basic, surface oxygen on CeO$_2$ has been considered a main anchor site for HA. Adsorption on CeO$_2$/13X is mainly governed by 13X. Again, TEA is hardly adsorbed and HA is adsorbed strongest among the VOCs.

In summary, it was found that for linalool and HA the mass deposition was additive for mixture with H-ZSM-5 and 13X whereas for the reactive limonene the mass gain onto mixed materials was higher than if compared to single (pure) support materials (see ESI SA9).

### 3.3.2 Evidence for catalytic oxidation

**One compound systems**

For CeO$_2$ an exothermic event $T_{\text{exo}}$ was found at 235 °C for the small molecules diethylether and at 180 °C for TEA. For limonene, a broad temperature range between 140-180 °C was measured. Limonene is probably partially oxidized when deposited generating a mixture of compounds on the support. These chemically different groups of intermediates might be further oxidized in different manner to CO$_2$ and water within the mentioned temperature range. Linalool and HA reacted at about 180 °C. Their hydroxyl functionality are probably deprotonated on the surface of ceria and these molecules have been reported to easily undergo nucleophilic activation [64]. On **H-ZSM-5** the exothermic peak of all VOC is situated between 230 and 260 °C. Compared to pure CeO$_2$, the reactions of TEA, limonene, linalool and HA are even delayed with respect to the other compounds. On 13X $T_{\text{exo}}$ lies between 300 °C and 350 °C for diethylether, TEA and limonene. On the contrary, for linalool and HA, the exothermic peak starts at much lower temperature. This could be indicative for the importance of hydroxyl
groups in the adsorbed molecules for activation. According to the Eley-Rideal-Model, the stronger the interaction of the molecule, the faster the reaction is [121]. However, for HA $T_{e\text{xo}}$ is extended over a large temperature range (220 - 325 °C) which might indicate an additional mechanism. Possibly HA is not only captured in the pores, but stays also on the outer surface or is progressively emitted. Here progressive oxidation may take place over a broad temperature range.

**Mixed CeO$_2$/zeolite systems**

For CeO$_2$/H-ZSM-5 the exothermic peak comes early for diethylether, TEA and limonene and is extended over a large temperature range. This might rise from combustion on CeO$_2$ after release from adjacent H-ZSM-5. Differently, linalool and HA have a $T_{e\text{xo}}$ between 230 and 250 °C. The combustion peak remains almost unchanged for linalool whereas for HA a significantly lower temperature is observed on mixed systems than if compared to pure H-ZSM-5. Here, again two classes of compounds are evident: aprotic diethylether, TEA and limonene and protic linalool and HA. On CeO$_2$/13X, $T_{e\text{xo}}$ is mainly governed by 13X and similar processes as for pure 13X are observed. However, HA now has a sharp $T_{e\text{xo}}$ at 230 °C as it was also observed for CeO$_2$/H-ZSM-5, indicative for a light-off phenomenon (oxidation is highly exothermic; see ESI SA6). This again supports the hypothesis that the combustion of HA mainly happens on CeO$_2$. Combining this observation and the behavior of HA on 13X calc. (prolonged combustion) it can be assumed that part of HA is emitted unaltered from its storage location on 13X and combusted by adjacent CeO$_2$. This may also explain the shift in $T_{e\text{xo}}$ of about 40 °C (mixture vs. pure CeO$_2$). Finally, it was found that basic supports like CeO$_2$ and 13X are more active towards linalool and HA. Mixing 13X with CeO$_2$ resulted in a sharp exothermic event for HA and slightly lowered the combustion temperature. Moreover, it can be noticed, that for limonene, linalool and HA the lowest $T_{e\text{xo}}$ is found on CeO$_2$ (see ESI SA9 where $T_{e\text{xo}}$ is plotted against the support material). Exothermic events are additive for HA and linalool (on H-ZSM-5, CeO$_2$/H-ZSM-5 and CeO$_2$).
Table 3.1 Physicochemical data of compounds used in this study

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<td>630.5</td>
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* Kinetic diameter σ[A] calculated according to 2.44(T_c/p_c)\(^{1/3}\)[127-130].  
* Kinetic diameter σ[A] calculated according to 1.234(M_w)\(^{1/3}\)[127]

3.3.3 Gas phase VOC model compounds

In order to assess the ability of the here discussed physical mixtures to capture representatives VOC and release them at a temperature where CeO\(_2\) is an active oxidizer for the compound, gas phase adsorption experiments were performed. Here, often a larger quantity of the VOC was adsorbed on the support material as in wet adsorption experiments (see ESI Table SA3). No competition for adsorption sites must be considered as in the case of diethylether during wet impregnation experiments. Figure 3.2 shows the differential thermo analysis plots and the MS traces for characteristic marker fragments and for CO\(_2\) (m/z = 44) during heating, as described in the experimental section. Adsorbed linalool on ceria was oxidized at around 180 °C. This is represented by an exothermic peak in the DT analysis (see Fig. 3.2 and 3.3) and CO\(_2\) evolution. On H-ZSM-5, a small exothermic peak was visible at 270 °C. In the same
temperature range it was preceded by a strong evolution of an m/z = 41 ion (C₃H₅⁺, a characteristic fragment for linalool). The CO₂ evolution started from 150 °C and continued up to 400 °C as CO₂ was progressively released. This might be indicative for a partial combustion in or on the zeolite itself. On CeO₂/H-ZSM-5 a shift of 80 °C up to 260 °C for Tₐ was observed. The linalool marker fragment (m/z = 41) dramatically diminished and CO₂ strongly evolved starting from about 175 °C up to 350 °C. This behavior may be described as an adsorption/capture release oxidation process (suggested acronym ACROP) and is similar to NOₓ storage catalysis or classical three way catalysis in modern automotive exhaust, where oxidation equivalents are intermediately stored on ceria. Linalool adsorbed on CeO₂/H-ZSM-5 is captured predominantly in the zeolite. When the sample is heated, the compound escapes presumably unaffected by the zeolite. This happens at a temperature where the oxidative catalyst (CeO₂) is active; hence oxidization of the released VOC takes place. This process is described in Scheme 3.3.

![Figure 3.2: Comparison between pure component and physical mixture (CeO₂, H-ZSM-5, 1:1 mix) for gas phase VOC adsorption and oxidation.](image)
Scheme 3.3: Suggested adsorption/capture release and oxidation process (ACROP). **a)** At room temperature VOC are collected on the adsorber (absorption/capture). **b)** When the absorber material is regenerated (higher temperature), adsorbates are released and are totally oxidized on adjacent ceria (release and oxidation). **c)** If the adsorbates were released before ceria reaches its working temperature (200 – 300 °C), captured VOC may be released again. (Dimensions are not in scale)

Apparently, according to DTA measurements, a similar process as described above partially takes place for limonene. An exothermic peak is observed very early at 140 °C on CeO₂ and CO₂ peaks at a similar temperature. Unreacted limonene is released in this temperature range (around 105 °C). Furthermore, a very little peak is visible at 270 °C on H-ZSM-5 and the mixture CeO₂/H-ZSM-5 yields a strong DTA signal at around 260 °C. The CO₂ evolution on CeO₂/H-ZSM-5 happens in two stages which clearly supports the above formulated ACROP hypothesis. A first peak originates from compounds oxidized on CeO₂ or H-ZSM-5 (as observed on CeO₂ and H-ZSM-5 alone). The second peak overlaps with the DTA signal at 260 °C (delay of 120 °C) and is indicative for the VOC liberated at high temperature and subsequently oxidized by ceria.
Figure 3.3: Comparison between pure VOC components in contact with pure zeolite 13X and physical mixtures (1:1 mix) using gas phase exposure of the solids in a fixed bed. For pure CeO$_2$ data, see Figure 3.2.

However, no strong marker signal evolution was observed for limonene on H-ZSM-5 as it was for linalool. TEA was adsorbed on CeO$_2$ only in little amount and yielded a small peak at 180 °C accompanied by a CO$_2$ evolution in the same temperature range. No clear exothermic peak was visible on H-ZSM-5. However, CO$_2$ evolved starting from 130 °C and was progressively released up to 400 °C. The combination of CeO$_2$ and H-ZSM-5 resulted in a stronger exothermic peak at 170 °C and at 240 °C with corresponding CO$_2$ evolution. The fact that CO$_2$ evolves in the same temperature range on pure CeO$_2$ and on CeO$_2$/H-ZSM-5 indeed suggests, that TEA combustion predominantly happens on ceria rather than on H-ZSM-5.

Linalool on 13X yielded a sharp exothermic peak at around 210 °C followed by a smooth decrease up to 350 °C (see Fig. 3.3). At similar temperature a very small signal in MS traces was visible, indicating intact (non-polymerized or oxidized) linalool. Carbon dioxide evolution again overlapped with the exothermic peak in DTA.

Mixed CeO$_2$/13X gave rise to two peaks in DTA. The first peak T$_{exo}$ was slightly shifted to lower temperature compared to pure 13X, but delayed with respect to pure CeO$_2$. The second peak T$_{exo}$ was situated at 250 °C and continued up to 350 °C. The CO$_2$ MS trace increased sharply at the same temperature (shoulder) and peaked at 250 °C. A continuous decrease of CO$_2$ was observed up to 350 °C and ended sharply when heating stopped at 460 °C (not shown). This behavior might be interpreted as following: the DTA peak at 195 °C probably originates from linalool directly adsorbed on CeO$_2$ (DTA peak on pure CeO$_2$ ranges up to 250 °C and displays a shoulder at 220 °C) while the peak at 250 °C might be a combination of decomposed
linalool on 13X directly and on CeO₂ upon release from the zeolite. For limonene, no exothermic peak was measured on 13X up to 400 °C. Additionally the MS marker (m/z = 68) and CO₂ evolution were very weak. On CeO₂/13X an exothermic peak was visible at 210 °C. Here, the limonene marker was found at around 110 °C. Carbon dioxide was formed at three stages: 105, 200 and 270 °C. This observation suggests an early decomposition of the test compound, even at very low temperature accompanied by intact desorption. However, as mentioned before, it is important to remind that limonene is easily oxidized even at room temperature. This could lead to formation of side products which decompose at different temperatures. For TEA the DTA signal showed a peak at around 280 °C with a shoulder at 350 °C on 13X. No TEA fragments were recorded by the MS system. Beside a very flat peak at 165 °C, this DTA signal corresponded to CO₂ evolution in the MS traces. On CeO₂/13X TEA gave rise only to one peak at 290 °C, accompanied by CO₂ evolution.

3.3.4 Effect of calcination

The effect of milling and calcination has been investigated on 13X using TEA as a model compound. TG and DTA showed a major mass loss for calcined 13X (-14.6%) in contrast to untreated 13X (minus 6.4%, see Fig. 3.4). The endothermic DTA signal indicates desorption processes in calcined 13X ranging from 20 °C up to 250 °C. Mass spectrometric analysis (not shown) confirmed (expected) loss of water. The untreated 13X, however, displays a less pronounced endothermic peak over the same temperature range, in line with reduced mass loss. Additionally, a small exothermic event can be observed between 100 and 200 °C.

![Figure 3.4: Relative mass loss (left) and differential thermo analysis (right) of pure 13X as-purchased and after calcination at 500 °C for 1h in air.](image)

Both calcined and untreated 13X were exposed to TEA in wet impregnation experiments (as TEA solution in diethylether). A higher loading (11 wt. %) was chosen in order to better highlight the involved processes. Exothermic peaks were observed on untreated 13X (see Fig. 3.5) at 290 °C and at 345 °C. Calcined 13X, however, showed only one weaker peak around
305 °C. The two peaks in untreated 13X indicate the presence of two types of adsorption sites for TEA or reminders from synthesis. The single peak on 13X calc. suggests a significant loss of adsorption sites and capacity.

Figure 3.5: Relative mass loss (left) and differential thermo analysis signal (right) of triethylamine after wet impregnation (in diethylether) for 13X as-purchased and after calcination at 500 °C for 1 h in air.

Nitrogen physisorption analyses of materials used in this study (see Table 3.2) indicate limited changes in BET surface area for calcined zeolites. However, as sample preparation for BET measurement involved desiccation, the relevant water content in 13X calc. may be responsible for capacity loss in calcined 13X.

Table 3.2 Nitrogen gas physisorption analysis of materials used in this study

<table>
<thead>
<tr>
<th>Support</th>
<th>Langmuir surface area [m²/g]¹</th>
<th>BET surface area [m²/g]¹</th>
<th>Micropore area [m²/g]²</th>
<th>External surface [m²/g]³</th>
<th>Pore volume [cm³/g]⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5 (a. p.)</td>
<td>502</td>
<td>384</td>
<td>223</td>
<td>162</td>
<td>0.256</td>
</tr>
<tr>
<td>H-ZSM-5 (calc.)⁵</td>
<td>460</td>
<td>372</td>
<td>222</td>
<td>110</td>
<td>0.289</td>
</tr>
<tr>
<td>13X (a. p.)</td>
<td>574</td>
<td>451</td>
<td>386</td>
<td>65</td>
<td>0.269</td>
</tr>
<tr>
<td>13X (calc.)⁵</td>
<td>576</td>
<td>470</td>
<td>342</td>
<td>59</td>
<td>0.328</td>
</tr>
<tr>
<td>CeO₂ (a. p.)</td>
<td>90</td>
<td>67</td>
<td>3.2</td>
<td>64</td>
<td>-</td>
</tr>
<tr>
<td>CeO₂/H-ZSM-5 (calc.)</td>
<td>265</td>
<td>202</td>
<td>96</td>
<td>106</td>
<td>0.189</td>
</tr>
<tr>
<td>CeO₂/13X (calc.)</td>
<td>218</td>
<td>168</td>
<td>100</td>
<td>68</td>
<td>0.195</td>
</tr>
</tbody>
</table>

¹ error +/- 5 %, ² measured on a TriStar II 3020, ³ single point adsorption

Additionally, the pore volume has been considered for VOC adsorption. We observe, that calcination increases pore volume by 13 and 22% in H-ZSM-5 and 13X, respectively. The pore volumes of the mixed phases correspond to 65 and 60% of the single phase, respectively. The
adsorption capacity was found to be proportional to the pore volume for linalool and disproportional for limonene and triethylamine when adsorbed on pure H-ZSM-5 and 13X (see Table 3.2, ESI Table SA3 and Figure SA15). Some correlation is found for adsorption capacity and external surface in the case of limonene and triethylamine. On pure phases, adsorption capacity was disproportional for linalool. At this point we suggest that the chemical structure, i.e. the functional groups present in the molecule of the VOC, are the governing forces for adsorption.

3.3.5 Regenerable oxidative adsorber

In order to test the bi-functional material mixture CeO\textsubscript{2}/13X (20/80 wt. %; calc. at 400 °C) as regenerable adsorber, breakthrough experiments were performed using TEA as an air pollutant model compound. The ability to adsorb TEA in an airstream has been tested with different combinations of CeO\textsubscript{2} and 13X (see Figure 3.6a). The best retention of TEA has been observed for untreated 13X (p = pelletized). Breakthrough of TEA, using CeO\textsubscript{2}/13X (50/50 wt. %) pellets (uncalcined) as adsorber material, started after about 30 min, whereas calcined material lost its adsorption ability already after about 20 min on stream. An even stronger adsorption ability loss was observed for 13X upon treatment. This behavior clearly shows that the processing (milling in water, calcination for 1 h at 500 °C) significantly reduced the adsorption capacity of 13X. As expected, the mass gain rate (defined as the mass increase of the adsorber at breakthrough divided by the time to breakthrough, see Table 3.3, mass gain rate\textsuperscript{c}) of all materials (except for pure ceria) is constant and is situated at around 1 mg/min. Taking into account the calculation and experimental deviations (\(\Delta = 15\%\)), this value is in line with the here chosen TEA loading and flow rates. This might suggest that the sites available for adsorption (more numerous for untreated materials) are occupied in the same way by TEA in both treated and untreated adsorber. The effect of reduced (milder) calcination temperature of the mixture CeO\textsubscript{2}/13X (20/80 wt. %) was tested for uncalcined material, and calcined at 400 °C and 500 °C (see Figure 3.6b). Additionally, model regeneration runs at 400 °C for 30 min in air were tested. Calcination at 400 °C again resulted in limited adsorption capacity (breakthrough already before 20 min). Regeneration, however, improved retention by more than a factor 2 (see Fig. 3.6b, trace Reg. 1). Even after a third run (see Fig. 3.6b, trace Reg. 2) retention of TEA remained unchanged. The poor initial adsorption performance of the material calcined at 400 °C and the subsequent improvement after regeneration, indicate an activation of the adsorber. Interestingly, the uncalcined support (dried at 65 °C, overnight) also showed an improved retention if compared to calcined material at 400 °C. A better retention capacity of uncalcined
material might actually derive from larger amounts of pre-adsorbed water in the matrix that acts itself as an absorber for TEA. Part of this water is removed at 400 °C (see Fig. 3.4 right) and an even larger part at 500 °C. In conclusion, the physical mixture of CeO$_2$/13X (20/80 wt. %) calcined at 400 °C could be successfully regenerated (400 °C, 30 min, in air) and reused. A fixed bed mass increase due to TEA adsorption of about 3% was measured and confirmed the previous experiments. TG-DTA measurements of 13X and CeO$_2$/13X (20/80 wt. %), both pelletized, were performed for fixed bed samples after breakthrough. As expected, less TEA adsorbed on CeO$_2$/13X if compared to 13X alone. The two DTA peaks partially coalesce when ceria is added (see Figure 3.7).

**Figure 3.6:** a) Adsorption experiments for model air contaminated with triethylamine (TEA) using pure CeO$_2$, pure 13X and intimate (sub-μm) mixtures. The fixed bed was flushed with contaminated model air (250 mL/min) containing TEA (460 ppmv, parts per million vol., corresponding to about 26 mmol/m$^3$). Except for pure CeO$_2$, all adsorber materials were in pellet form (200 – 400 μm). b) Regeneration test runs using CeO$_2$/13X (20/80 wt. %, calc. 400 °C) as a starting material and Reg. 1 and 2 as regeneration runs. For comparison CeO$_2$/13X (20/80 wt. %, uncalcined) and calcined at 500 °C are included.
Table 3.3 Adsorption experiments using fixed beds and 460 ppmv triethylamine in air

<table>
<thead>
<tr>
<th>Support</th>
<th>GHSV [h⁻¹] b</th>
<th>t_B [min]</th>
<th>Mass gain rate [mg/min] c</th>
<th>Mass gain rate [mg/min] d</th>
</tr>
</thead>
<tbody>
<tr>
<td>13X (uncal., p)</td>
<td>5400</td>
<td>118</td>
<td>0.94</td>
<td>0.49</td>
</tr>
<tr>
<td>CeO₂/13X (1:1 mill calc. p)</td>
<td>6500</td>
<td>15</td>
<td>0.98</td>
<td>0.02</td>
</tr>
<tr>
<td>CeO₂/13X (1:1 mix uncalc. p)</td>
<td>8800</td>
<td>30</td>
<td>1.1</td>
<td>0.20</td>
</tr>
<tr>
<td>CeO₂/13X (20/80 mix uncalc. p)</td>
<td>4900</td>
<td>90</td>
<td>1.1</td>
<td>0.48</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1600</td>
<td>&lt; 37</td>
<td>(0.23) e</td>
<td>-</td>
</tr>
<tr>
<td>13X (calc., p)</td>
<td>8800</td>
<td>&lt; 20</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a p = pellets of 200 – 400 μm size, b Flow 250 mL/min, variable bed height, t_B = time to breakthrough (1 cycle), c mass gain/t_B, d mass gain from breakthrough/(150 min - t_B), e very short adsorption time results in large error, GHSV = gas hourly space velocity.

Figure 3.7: Relative mass loss (left) and differential thermo analysis signal (right) of materials (unmilled and uncalcined) exposed to triethylamine containing air on fixed beds after breakthrough.

3.4 Conclusion

The combination of storage and catalytic oxidation in a single granular material is attractive for the energy efficient removal of VOC in high air volume applications as it combines regeneration capability (low maintenance costs and material requirements) and reduced air heating or cooling costs. Both benefits are particularly clear if the here outlined process is compared to direct air exchange (the whole air volume must be heated or cooled to indoor conditions), or adsorption on conventional (single use) activated carbon. Since physical mixtures can be easily prepared from a broad variety of oxidation catalysts and suitable zeolites or other microporous materials, the concept of capture/storage – release and oxidation may become useful in a number of gas treatment processes, where a minor contaminant must be removed from large volumes under energy sensitive conditions.
4. Indoor air purification using activated carbon adsorbers: regeneration using catalytic combustion of intermediately stored VOC

Accepted publication:
4.1 Introduction

People spend almost 80% of their time indoors. This might have a significant impact on human health when the air is contaminated with air pollutants (APs) [131, 132]. Typical APs are represented by volatile organic compounds (VOC) [133], particulate matter [134] and volatile oxides such as NOx [135], SO2 and CO [136]. Hence, ensuring good indoor air quality is a challenge both in public and in private buildings as these AP have different characteristics including volatility, polarity and size. Current air purification technologies rely on heating, ventilating and air conditioning systems (HVAC), photo catalytic oxidation [33, 82-84] or filtration via activated carbon [79-81].

HVAC systems are energy intensive as large air volumes have to be exchanged (typically three times the room volume per hour), filtered and cooled or heated (note the heat capacity of air: 1.2 kJ/m³ and per °C) [116]. Additionally, frequent maintenance is required as these systems are complex and adsorbers are often used only once. Even though, progress is made in HVAC systems technology by using e. g. activated carbon fiber filters [137], these systems still account for 50% of building energy consumption (20% of total consumption in US) [23]. Alternative technologies, where photo catalysis or ozone is used as oxidation strategy for removal of VOC, can release dangerous side products [15, 85]. Hence, in earlier studies we investigated the possibility to efficiently remove VOCs from air using ceria (CeO₂) based adsorber where the adsorber (for acidic VOCs) acts at the same time as an oxidative catalyst to enable thermal regeneration of the adsorber on site [116]. To extend such a two-step catalyst/adsorber concept to different classes of VOCs, we then combined the oxidative catalyst (CeO₂) with zeolites [138]. As mentioned before, however, activated carbon adsorbers are most frequently used. When the activated carbon adsorber is exhausted, it has to be replaced. Small quantities are usually disposed and burned. Thus, large environmental footprint results from maintenance and associated waste. Large quantities of exhausted activated carbon are regenerated in specialized plants. The material usually undergoes the following steps: drying at 105 °C, pyrolysis under inert atmosphere (500 – 900 °C) and gasification of residues by oxidizing gases (e. g. steam or CO₂) [37]. For domestic applications, this process is too expensive. To significantly reduce energy, material and maintenance costs, in situ regeneration of activated carbon (AC) is required. The regeneration of AC has been investigated over the last decade and include thermal- [37, 43, 45], ozone-[44], microwave assisted [139, 140], electrochemical- [141] and even supercritical CO₂ based [142] processes. Additionally, in situ adsorption-catalysis systems were investigated by Huang et al.[143].
In this work, an in situ regenerable AC/oxidative catalyst system (Scheme 4.1) that is more relevant for domestic use was investigated. A two-step approach using representative VOCs and commercially available activated carbon (AP4-60) were used. As oxidative catalyst a mixture of CeO$_2$/TiO$_2$ nanoparticles was chosen since ceria is a wide spread oxidative catalyst. TiO$_2$ was used as binder for pellets formation. In the first step VOCs are removed from the air by adsorption at room temperature. In the second, regenerative step the VOCs are released from the carbon part of the system at higher temperature in an air stream, and catalytically combusted on the adjacent catalyst bed. This system potentially has an additional advantage, as very polar VOCs (e.g. formic acid) that would be hardly captured by AC may adsorb on cerium oxide for subsequent oxidation. Rankovic et al. studied a similar process using AC as adsorber and Pt/Al$_2$O$_3$ as catalyst for combustion of xylene and SOLVESSO 100 (solvent mixture C9 - C10 dialkyl and trialkyl benzenes, bp. 165 – 181°C) [144]. The use of noble metals such as platinum for catalysis was deliberately avoided in order to minimize material costs. As catalytic activity is related to accessible surface area, possible aging for catalyst with dispersed metals may arise from surface area loss by sintering of metal particles whereas the cerium oxide catalyst has virtually no aging at the used temperature [58, 116]. Kullavanijaya et al. investigated the co-adsorption of thiophene–containing mixtures and their subsequent desorption and oxidation over Pd/CeO$_2$/Al$_2$O$_3$ [145]. In contrast to their work we aimed to investigate air pollutant with much lower volatility that requires higher regeneration temperature for AC. Hence, the effect of regeneration on activated carbon was investigated more in detail.

### 4.2 Experimental section

**Materials.** Activated carbon (AC, AP4-60) was purchased from Chemviron Carbon, Germany (L = 5 – 10 mm, D = 4 mm, m = 35 – 75 mg, max. moisture 5 wt. %, max. ash 14 wt. %). After crushing, the sieve fraction from 200 – 400 μm (Filtravibración S. L. AISI 304 stainless steel) was selected for further experiments. Cerium oxide (CeO$_2$) (15-30 nm APS, 99.5% purity, 30-50 m$^2$/g specific surface area, SSA) was purchased from Nanostructured & Amorphous Materials Inc. Texas, USA and mixed in a 50 wt. % mixture with titanium oxide (binder) nanoparticles (Aeroxide TiO$_2$ P25, Evonic). The powder mixture was compressed and pelletized, crushed and sieved as explained before. Activated carbon was loaded with following test compounds: (±)-linalool (Fluka, purum), triethylamine (TEA, Aldrich, 99.5%), S-(−)-limonene (Fluka, 99% GC) and hexanoic acid (HA, Aldrich, 99%), diethylether (Sigma-Aldrich, ≥ 98.5% GC) and n-decane (Sigma-Aldrich ReagentPlus ≥ 99%).
**Methods.** The adsorber material was exposed for preliminary studies to a saturated VOC atmosphere. In a closed plastic tube (Techno Plastic Product AG, TPP, 50 mL) a small glass bottle (Fiolax, 5 mL) containing AC was placed. Outside the glass bottle, 2 mL of the liquid model compound were poured. After exposure, samples were ventilated at room temperature for about 30 min and subsequently analyzed by thermogravimetry (TG, Linseis TG/STA-PT1600) under air (6 L/h) from 20 to 450 °C (heating rate of 10 °C/min). The gas stream from the instrument was directly analyzed with a mass spectrometry system (MS, OmniStar™ GSD 320, 60 eV, 1-100 amu, 0.1 s/amu scan time) to identify desorption and decomposition products. Adsorption and desorption cycles were performed as following: a reservoir vessel containing the VOC (TEA, n-decane or limonene) was flushed with compressed air (80 mL/min for TEA (at 24 °C) and 250 mL/min for n-decane and limonene (liquid maintained at 40 °C)). The concentration in the inlet stream was determined gravimetrically by measuring the mass loss over time and the air flow through the vessel. The VOC loaded air was passed through an AC fixed bed. Breakthrough was monitored in-line with a MS system. Regeneration was done in a tubular oven at 450 °C in an air stream (20 mL/min) until no marker signal was detected in the off-gas stream. AC was characterized as following: the specific surface area (SSA) was determined on a Tristar Micromeritics device (Norcross, GA, USA) with nitrogen at 77 K after desiccation for 4 h at 573 K. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were collected on a Tensor 27 (Bruker) spectrometer equipped with a PIKE DiffuseIR accessory. Spectra were collected from 4000 to 400 cm⁻¹ using a 5 wt. % KBr mixture. Elemental compositions were determined with a Vario MICRO cube (Elementar Analysensysteme GmbH) in the CHNS mode.

### 4.3 Results and Discussion

**Thermal behavior of blank AC.** Activated carbon was heated in the TG-DTA-MS device in an air stream up to 1000 °C. A strong exothermic peak was monitored between 500 and 650 °C accompanied by water and CO₂ evolution as seen in the MS traces (m/z = 44 and 18 in Figure 4.1). A mass loss of only 2.5 wt. % was measured up to 450 °C indicating no significant degradation of AC up to this temperature. This mass loss was attributed to moisture, residual adsorbates but only marginally to carbon loss.
Accordingly, all regenerations were done below this temperature. The outer surface of AC was analyzed by DRIFTS (Figure 4.2). A band at 3420 cm$^{-1}$ is attributed to O–H stretching vibration indicating that the here used AC is partially oxidized. This can be traced back to the activation process. IR-bands measured at 1385 cm$^{-1}$ and 1635 cm$^{-1}$ are attributed to $-\text{O}=$C–O and $-\text{C}=\text{C}$ [40, 146] or $-\text{CH}$ [147] groups, respectively.

**Figure 4.2:** Diffuse reflectance infrared absorption spectroscopy (DRIFTS) of AP4-60 blank. Signals found at 3420 cm$^{-1}$ is attributed to hydroxyl groups whereas the signals found at 1385 cm$^{-1}$ and 1635 cm$^{-1}$ correspond to C–O stretch vibration (conjugated C=O or carboxyl) and $-\text{C}=\text{C}$, respectively [40, 146].
Preliminary gas phase adsorption and desorption experiments. The desorption process was monitored in a TG-DTA-MS system (Figure 4.3 and 4.4). Results are listed in Table 4.1 and 4.2. In preliminary experiments the VOC amount adsorbed was between 1.5 and 2 mmol/g. Linalool and hexanoic acid needed higher temperature and longer exposure times for saturation as they have much lower partial pressures (0.1 and 0.3 mbar at 20 °C for linalool and hexanoic acid respectively) compared to the other compounds. Considering the BET surface area of 1150 m²/g the coverage corresponds to about 1 molecule per nm² for all VOCs and suggests a monolayer-type adsorption after taking into account the cross section of the adsorbed VOCs [148-150]. The amount measured for TEA (2.07 mmol/g) may be a combination from TEA, moisture and CO₂ capture [151, 152]. This observation is in agreement with the stronger m/z = 18 and 44 signals found for TEA in MS analysis upon thermal regeneration (Figure 4.4). Additionally, it can be noticed that for limonene, linalool and HA the weight loss continues (moderately) even after complete VOC desorption according to MS traces (Figure 4.3, right). Except for diethylether, an exothermic peak was visible during desorption for all samples which corresponded to the highest mass loss rate in TG.

Figure 4.3: Thermogravimetric (top) and differential thermo analysis (bottom) of gas phase adsorbed VOCs on AP4-60 granules (200 – 400 μm). Mass loss is associated with desorption of VOC. Exothermic processes, visible in the DTA plots (below), are associated with oxidation of VOC or AC.
Table 4.1. VOC adsorption experiments and quantitative changes in composition

<table>
<thead>
<tr>
<th>Compound</th>
<th>TG</th>
<th>Δm$_{400°C}$</th>
<th>T$_{exo}$ [°C]</th>
<th>Intact desorption [°C]</th>
<th>C[%]</th>
<th>H[%]</th>
<th>N[%]</th>
<th>%Δm [total]</th>
<th>%ΔΔm [H]$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP4-60 blank (*)</td>
<td>2.2</td>
<td>-</td>
<td>83.0</td>
<td>0.67</td>
<td>0.20</td>
<td>15.9</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyether$^a$</td>
<td>11.9</td>
<td>-</td>
<td>100 - 200</td>
<td>80.9</td>
<td>2.16</td>
<td>0.19</td>
<td>16.4</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>TEA$^b$</td>
<td>19.5</td>
<td>205</td>
<td>80 - 220</td>
<td>79.2</td>
<td>3.55</td>
<td>3.23</td>
<td>13.2</td>
<td>2.88/3.03$^d$</td>
<td></td>
</tr>
<tr>
<td>HA$^c$</td>
<td>18.7</td>
<td>240 / 340</td>
<td>120 - 350</td>
<td>79.5</td>
<td>2.43</td>
<td>0.4</td>
<td>17.2</td>
<td>1.76</td>
<td></td>
</tr>
<tr>
<td>limonene$^b$</td>
<td>22.3</td>
<td>270 / 330</td>
<td>100 - 300</td>
<td>85.0</td>
<td>3.85</td>
<td>0.14</td>
<td>10.7</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>linalool$^c$</td>
<td>23</td>
<td>265</td>
<td>100 - 320</td>
<td>80.6</td>
<td>3.62</td>
<td>0.2</td>
<td>15.4</td>
<td>2.95</td>
<td></td>
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<tr>
<td>n-decane$^b$</td>
<td>24</td>
<td>350</td>
<td>80 - 350</td>
<td>84.0</td>
<td>4.25</td>
<td>0.16</td>
<td>11.3</td>
<td>3.58</td>
<td></td>
</tr>
</tbody>
</table>

* (AC), $^a$ 38 h adsorption at room temperature, $^b$ 28 h adsorption at 50 °C, $^c$ 6 days adsorption at 70 °C, $^d$ % Δm [N], $^e$ blank H [%] value subtracted from H [%] of AC/VOC

As desorption is an endothermic process, the energy produced is attributed to partial combustion of fine dispersed VOCs on the large surface area of the adsorber or partially oxidation of the AC. For limonene a whole range of fragments was recorded that did not fit the database (Spectra Database for Organic Compounds, SDBS) values corresponding to intact limonene (see ESI Figure SB1). Possibly, these fragments belong to polymerized or oxidized derivatives of limonene [123-125]. The desorption temperature was found to correlate with the boiling points of the used compounds (Figure 4.4).
Figure 4.4: Mass spectrometry analysis of VOC desorption from AP4-60 granules (200 – 400 μm) during temperature programmed desorption (TG). Marker ions indicate intact desorption of VOCs. CO₂ and H₂O (m/z = 44, 18) evolution is associated to combustion processes. Desorption temperatures are summarized in Table 1.

Hence, a low desorption temperature is associated with a weak adsorption strength and corresponds to, following order: diethylether < TEA < n-decane < limonene < linalool < HA. This is in agreement with adsorption strength measured by Kullavanijaya et al. where diethyamine adsorbed much weaker on activated carbon than cyclohexane, thiophene and methyl-metacrylate [145].
Table 4.2. Comparison between thermogravimetric and elemental analysis data

<table>
<thead>
<tr>
<th>Compound</th>
<th>TG analysis mmol/g AC Δn&lt;sub&gt;800 °C&lt;/sub&gt;</th>
<th>Elemental analysis mmol/g AC Δn&lt;sub&gt;400 °C&lt;/sub&gt;</th>
<th>Ratio TG/E</th>
<th>Cross section [Å&lt;sup&gt;2&lt;/sup&gt;]</th>
<th>Coverage molecule/nm&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP4-60 (*) blank</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diethylether&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.39</td>
<td>1.49</td>
<td>1.07</td>
<td>42</td>
<td>0.72</td>
</tr>
<tr>
<td>TEA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.07</td>
<td>1.92/2.16</td>
<td>0.93/1.04</td>
<td>43</td>
<td>1.1</td>
</tr>
<tr>
<td>HA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.7</td>
<td>1.49</td>
<td>0.87</td>
<td>57&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.78</td>
</tr>
<tr>
<td>limonene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.85</td>
<td>1.99</td>
<td>1.07</td>
<td>58&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.96</td>
</tr>
<tr>
<td>linalool&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.7</td>
<td>1.64</td>
<td>0.96</td>
<td>58&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.86</td>
</tr>
<tr>
<td>n-decane&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.96</td>
<td>1.63</td>
<td>0.84</td>
<td>86</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* (AC), <sup>a</sup> 38 h adsorption at room temperature, <sup>b</sup> 28 h adsorption at 50 °C, <sup>c</sup> 6 days adsorption at 70 °C, <sup>d</sup> estimated from isopropylhexane [150], <sup>e</sup> estimated from n-heptane [150], <sup>f</sup> calculated from N content

Elemental analysis revealed a carbon content for AP4-60 of 83% and very low content of H, N, and S (Table 4.1). The difference in total mass of 15.9% is attributed to oxygen and ash. According to the manufacturer, the ash content is maximally 14 wt. % resulting in an estimated oxygen content of at least 2 wt. %. However, thermogravimetric analysis revealed a residual mass of 6% at 800 °C. Assuming latter to be ash, the remaining 9.9% may be attributed to oxygen and is in qualitative agreement with IR data. The elemental analysis showed a clear increase in H content for all samples after gas phase VOC adsorption. Additionally, TEA adsorbed on AC was confirmed by an increase in the measured N content. The loadings calculated from TG and elemental analysis are in good agreement for diethylether, limonene, TEA and for linalool (Table 4.2). For n-decane the deviation is about 16% and for HA 13% (Table 4.2). These data indicate, that the desorption of VOC was complete at 400 °C as MS traces suggest.

**Adsorption and desorption cycles.** The results are summarized in Table 4.3. The weight of the whole fixed bed was recorded after loading and after regeneration. In Figure 4.5 the breakthrough curves measured by MS are shown. Generally, breakthrough started earlier after 4 cycles in comparison with the initial retention time. This might be due to fixed bed restructuring and loss in surface area. The adsorption capacity was found to be on average 28.7 wt. % for TEA, 38.3 wt. % for n-decane and 38.2 wt. % for limonene. This is comparable to data found in the literature [153, 154].
Table 4.3. Adsorption and regeneration cycle for selected VOC

<table>
<thead>
<tr>
<th>VOC</th>
<th>Cycle</th>
<th>Capacity [%]</th>
<th>AC loss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA a</td>
<td>1</td>
<td>29.9</td>
<td>-0.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>29.8</td>
<td>-2.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>27.8</td>
<td>-0.1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>27.3</td>
<td>-0.3</td>
</tr>
<tr>
<td>n-decane b</td>
<td>1</td>
<td>35.7</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>39.1</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>38.3</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>40.0</td>
<td>9.0</td>
</tr>
<tr>
<td>limonene c</td>
<td>1</td>
<td>39.4</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>38.3</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>39.2</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>35.7</td>
<td>21.9</td>
</tr>
</tbody>
</table>

* a activated carbon was 500 mg, 80 mL/min, C_{in} ≈ 13000 ppm;  
  * b activated carbon was 250 mg, 250 mL/min, C_{in} ≈ 2000;  
  * c activated carbon was 250 mg, 250 mL/min, C_{in} ≈ 1700 ppm;  
  * d calculation based on corrected mass of residual AC after regeneration (raw data see ESI)

Figure 4.5: Mass spectrometry monitoring of breakthrough of VOC from AP4-60 granules (200 – 400 μm) (example of 2nd cycle).

While the adsorption capacity slightly decreased for TEA and limonene after 4 cycles, an increase was observed for n-decane. The VOC desorption was found to be complete according to mass loss and MS monitoring of marker ions in regeneration runs. However, the
mass loss was found to be a combination of desorbed VOC and loss of AC. This was more pronounced for limonene and \( n \)-decane, whereas in experiments with TEA the carbon mass loss was very small. In contrast to our results, Rankovic et al. found a much stronger AC mass loss when desorbing solvents in air (AC used was K81/B, Trayal Corporation, Kruševac). Starting from 120 °C up to 280 °C the mass loss reached almost 20%. To overcome this, a nitrogen atmosphere was used. The much lower decomposition temperature might be a result of catalytic active metal oxide constituting the ash portion of the AC. However, this hypothesis needs to be evaluated carefully by analyzing the residual ash of both activated carbons mentioned (AP4-60 and K81/B).

**Effect of thermal regeneration.** Elemental compositions of regenerated AC were measured after four TEA, \( n \)-decane and limonene adsorption and desorption cycles. The carbon content (Table 4.4) decreased after 4 regeneration cycles from 83% to 75.8% (TEA), 69.4% (\( n \)-decane) and 62.7% (limonene). Despite a residual N content of 1.6%, which is attributed to inorganic nitrogen, the increase in mass (%ΔΔm [blank]) not corresponding to C, H, N and S is attributed to oxygen species generated during oxidation in air. Hence, an increased tendency for oxidation is observed in the following order for different VOCs: AC/limonene > AC/\( n \)-decane > AC/TEA.

**Table 4.4.** Elemental analysis of regenerated AC (4 cycles)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C [%]</th>
<th>H [%]</th>
<th>N [%]</th>
<th>S [%]</th>
<th>% Δm [total]</th>
<th>% ΔΔm [blank]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC/TEA</td>
<td>75.8</td>
<td>0.96</td>
<td>1.8</td>
<td>0.3</td>
<td>21.4</td>
<td>+ 5.5</td>
</tr>
<tr>
<td>AC/limonene</td>
<td>62.7</td>
<td>1.0</td>
<td>0.26</td>
<td>0.2</td>
<td>35.8</td>
<td>+ 19.9</td>
</tr>
<tr>
<td>AC/( n )-decane</td>
<td>69.4</td>
<td>0.95</td>
<td>0.4</td>
<td>0.3</td>
<td>29.0</td>
<td>+ 13.1</td>
</tr>
</tbody>
</table>

\(^a\) mass percentage not associated to C, H, N and S and assumed to contain largely oxygen and ash.

\(^b\) difference between % Δm [total] of AP4-60 blank (15.9% in Table 1) and % Δm [total] (in Table 4.4) and assumed to correspond to an increase in oxygen content.

Figure 4.6 (left) shows the \( \text{N}_2 \) adsorption isotherms of AP4-60 blank (200 – 400 μm) and after four adsorption/desorption cycles of VOC. A Langmuir type isotherm (Type I) is visible for all samples indicating monolayer nitrogen adsorption [155]. The micro pore size is situated below 2 nm in agreement with literature data [156]. The slightly enhanced hysteresis loop (H4 type) after regeneration cycles suggests an increased mesopore or macropore volume [155].
Figure 4.6: Nitrogen adsorption and desorption isotherms measured at 77 K (left) and pore size distribution plot (right). A loss in micropore area is visible from the initial part of the adsorption isotherms after four adsorption/desorption cycles.

BET surface area decreased by 20% (n-decane), 31% (TEA) and 37% (limonene) after 4 regeneration cycles (Table 4.5). Loss in micropore area and micropore volume (t-plot) was more pronounced (-36%, TEA; -50%, n-decane and -68%, limonene). The external surface increased during n-decane and limonene adsorption/desorption and decreased after TEA adsorption/desorption. The trend for micropore loss was confirmed by calculating the pore volume distribution based on total pore volume. Additionally, the difference between total pore volume and micro pore volume, which is assumed to correspond to meso and macro pore volume is increased compared to AP4-60 blank for AC/limonene and AC/n-decane and diminished for AC/TEA (Table 4.5). A decrease in micropore volume was observed in the following order: AC/limonene > AC/n-decane > AC/TEA. The oxidized state of the carbon surface is assumed to affect N₂ physisorption equally in all samples.
Table 4.5. N₂ physisorption after 4 cycles

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area [m²/g]</th>
<th>t-Plot micropore area [m²/g]</th>
<th>t-Plot external surface [cm²/g]</th>
<th>total pore volume [cm³/g]</th>
<th>t-Plot micropore volume [cm³/g]</th>
<th>ΔV [total – micro]</th>
<th>% micropore volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP4-60 blank</td>
<td>1150</td>
<td>741</td>
<td>409</td>
<td>0.641</td>
<td>0.374</td>
<td>0.27</td>
<td>58</td>
</tr>
<tr>
<td>AC/TEA</td>
<td>789</td>
<td>474</td>
<td>315</td>
<td>0.449</td>
<td>0.239</td>
<td>0.21</td>
<td>53</td>
</tr>
<tr>
<td>AC/limonene</td>
<td>717</td>
<td>238</td>
<td>480</td>
<td>0.441</td>
<td>0.117</td>
<td>0.32</td>
<td>26</td>
</tr>
<tr>
<td>AC/n-decane</td>
<td>925</td>
<td>373</td>
<td>553</td>
<td>0.547</td>
<td>0.183</td>
<td>0.36</td>
<td>33</td>
</tr>
</tbody>
</table>

**In situ catalytic combustion of released VOC.** After studying the regenerability of AC for different VOCs, the total oxidation of the released VOC on a CeO₂/TiO₂ catalyst was tested. Activated carbon was loaded with VOC (TEA, n-decane and limonene on 100 mg AC). Portions of 20 mg AC containing VOC were desorbed as described in Scheme 4.1. Desorption and subsequent oxidation process was performed in an air stream and monitored by mass spectrometry. The result show, that virtually all desorbed VOC are oxidized at 450 °C on the CeO₂/TiO₂ catalyst to carbon dioxide and water (Figure 4.7 (with cat.), note the logarithmic scale for the ion current). When TEA is oxidized the ion m/z = 46 increased indicating formation of NO₂ (see ESI B). It was confirmed that in absence of the oxidative catalyst the released VOC escapes in the atmosphere. Similar result were found by Kullavanijaya et al. using reduced Pd/CeO₂/Al₂O₃ [145].

**Scheme 4.1:** *Modus operandi* for the adsorber coupled with the oxidative catalyst. Adsorption of VOCs happens at room temperature. Regeneration at 450 °C releases previous adsorbed VOCs. At this temperature the oxidative catalyst (CeO₂/TiO₂) is active for catalytic combustion.
Figure 4.7: Desorption and catalytic combustion of limonene. During desorption in presence of CeO$_2$/TiO$_2$ catalyst, no or very limited VOC was detected in the exhaust indicating successful total oxidation upon release (data for TEA and $n$-decane are available in ESI B).

**Capital and operational costs.** For a capital cost estimation we considered the material costs (AC, oxidative catalyst), the service costs and the regeneration of AC. Assuming an average concentration of indoor VOC of 0.5 ppm (equals 2.6 mg/m$^3$ for an average molecular weight of 130 g/mol) [157] and an AC adsorption capacity of 20 wt. %, this would correspond to 200 g VOC/kg adsorber. For an average room volume of 50 m$^3$ (total VOC about 130 mg) this would correspond to about 1540 room volumes per kg adsorber and would last for about 21 days (for 150 m$^3$/h air circulation). At this point the activated carbon must be replaced or regenerated separately. This will significantly increment the maintenance costs due to replacement or regeneration. Additionally, the environmental burden may increase as usually small amounts of AC are not reactivated but incinerated. From Table 4.6 it is visible, that the costs originating from frequent maintenance service represent the main expenses. However, the main costs still arise from the catalyst itself. There are at least two possibilities for decreasing costs: (1) increase activity or (2) increase surface area of the catalyst. (1) The use of noble metals such as Pt and Rh for activity enhancement is not amenable as a production on a large scale of noble metal doped air purifiers, like in catalytic converter, would further aggravate the global supply for such important raw materials. The use of these metals would be of much greater value if used in crucial chemical processes. The increase in activity may also be achieved by replacing ceria nanoparticles, which are dominated by (111) surfaces, with single-
crystalline nanocubes, displaying preferably the more oxidative (100) surfaces [62]. However, the production costs of ceria nanocubes may represent also a conspicuous part of the total costs. (2) An increase in surface area may be achieved by producing mesoporous ceria [75]. However, here as well the production cost of more sophisticated catalyst may increase the catalyst costs.

**Table 4.6.** Cost estimate for monthly regeneration (1.4 kg adsorber)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Material Cost [+]</th>
<th>Service costs [+]</th>
<th>Regeneration costs [d][c]</th>
<th>Catalyst cost [+]</th>
<th>Total cost for first year of operation [+]</th>
</tr>
</thead>
<tbody>
<tr>
<td>replacement</td>
<td>2.8</td>
<td>550 a</td>
<td>-</td>
<td>-</td>
<td>~ 553</td>
</tr>
<tr>
<td>replacement + off-site reactivation</td>
<td>2.8</td>
<td>550 a</td>
<td>68 c</td>
<td>-</td>
<td>620</td>
</tr>
<tr>
<td>replacement + in-situ reactivation</td>
<td>2.8</td>
<td>50 b</td>
<td>~ 1</td>
<td>150 d</td>
<td>~ 204</td>
</tr>
</tbody>
</table>

a assuming 11 material exchange and service per year (50 $/service); b assuming 1 service/maintenance per year; c assuming 4.4 $/kg reactivation; d material, shell and heater

The higher acquisition costs originating from the oxidative catalyst are already amortized after about one year. Hence, an *in situ* regenerable system would extend the service free time substantially, allowing conspicuous money and energy saving. The energy needed to desorb the accumulated VOCs and combust them catalytically is dominated by the heat capacity of used materials and is negligible if compared to running costs. Due to material loss found in regeneration cycles (average 5%) a halving of the AC is expected after 13 cycles. However, by decreasing the regeneration temperature (*e. g.* 400 °C) and prolonging the regeneration time, the used AC would last much longer as carbon loss would be further minimized.

**4.4 Conclusion**

In this study we combine a standard VOC adsorber (activated carbon) with an oxidative catalyst to provide an *in situ* regenerable air purifier system. The use of activated carbon allows the successful adsorption of a vast range of non-polar or weak polar VOCs. The downstream installed CeO2/TiO2 oxidative catalyst eliminates the released VOC during periodical thermal regeneration steps. This low-tech air purification system based on widespread materials allows considerable energy saving as heating power is only required during adsorber regeneration and catalytic combustion. Moreover, periodic maintenance by qualified staff is drastically reduced.
5. Conclusion

Conclusively, this work proposes three different strategies for indoor volatile organic compounds (VOCs) removal. CeO₂ nanoparticles have shown to be suitable for adsorption and catalytic combustion of acidic VOCs. Physical mixtures of zeolite, used as broad VOCs adsorber, and cerium oxide, used as oxidative catalyst, have proven to be applicable for adsorption/capture, release and oxidation also of non-acidic VOCs like linalool. Lastly, activated carbon, combined in series with an oxidative catalyst, was proven to be a suitable VOCs removal and in situ regenerable air purifier.

Even though the results showed to be very promising, these three different approaches indeed have limitations and a critical discussion seems to be appropriate and fair at this point. Concerns regarding safety, application site and associated limitations are discussed. Finally, possible manufacturing of a hypothetic final product is covered.

In our CeO₂ based air purifier, air was passed through the nanoparticle (NP) fixed bed. The question regarding emission of CeO₂ NP in the atmosphere arises, especially as these systems may be used in domestic fields where contact to people over an extended period is expected. The uptake and accumulation of CeO₂ NP in lung cells has been reported elsewhere [158]. In order to quantify the risk of indoor NP release during adsorption and regeneration steps, an analysis of exhaust air is required. This could simply be accomplished by scrubbing the air released in an appropriate solution and further analysis by ICP-OES or ICP-MS. To avoid a possible release of CeO₂ NP, appropriate immobilization is mandatory. Another point of concern that may arise, regards the amount of VOCs accumulated previous to regeneration. In our experiments loading of about 2 wt. % or 2.5 μmol/m² were reached and regeneration at temperatures of approximately 500 K were possible without any problem. If we assume the explosion limits of acidic VOCs to be between 1.3 vol. % and 9.3 vol. %, 1 kg adsorber (20 g VOC), a total desorption at 500 K within 30 s, an explosive mixture (flash point ~ 100 °C) given by a malfunctioning of the heating elements may be possible between 1000 L/min (LEL) and 150 L/min (UEL). Otherwise the mixture would be too rich or too lean. Hence, an ignition during regeneration runs is unlikely to happen if 150 L/min are not exceeded. On the other hand, the time for regeneration should be chosen in such a way that not enough VOC is accumulated that might represent a risk. A last important safety issue is represented by the possible formation of side products [58] in regeneration steps.

The application of such a purification system is best situated in an environment rich in acidic VOC. This would correspond for example to a kitchen, where thermo-oxidation of fatty acids, e. g. oleic or linoleic acid, occur during frying with vegetable oils [159, 160]. For
example, such conditions are frequently found in fast food restaurants. Also molecules having tertiary alcohols (linalool) or easy oxidizable functionalities (limonene) have shown to adsorb on CeO$_2$ [138]. In order to widen the range of VOCs suitable for adsorption on ceria a pre-oxidation of primary alcohols, terminal aldehydes and double bonds may be applied preliminary to the CeO$_2$ adsorber.

Finally, in order to allow implementation of such products on a large scale, manufacturing requirements have to be considered. The purpose is to sell a product at a target price of 150 $ (installation excluded). Simplified, the air purifier is made from 4 parts: adsorber material unit, cage, heating element (including control unit) and fan. Except of the adsorber material unit all other components are well established low cost commodities. Hence, focus is set on the adsorber material unit. Overall costs strongly depend on production methods, more precisely on the form of how the adsorber material is utilized: free powder or immobilized on large surface support. Since pressure drop and mass transfer problems may arise when a nanoscale powder is applied, this application form seems problematic. Additionally, the loss of NPs in the environment is probably likely to be relevant as mentioned before. In order to minimize pressure drop over the catalyst a well-established honeycomb ceramic monolith is appropriate as it is already used in the car industry. The monolith has to be coated with the adsorber/catalyst material, either by direct precipitation of ceria on the surface, or by wash coating, using previously synthesized ceria nanoparticles. As spray pyrolysis (SP) is a well-established technology able to produce materials up to megatons per year and direct precipitation may need several immersion/treatment steps, SP seems more suitable for a large scale production. The CeO$_2$ NPs are then immobilized on the support. Alternatively mesoporous high-surface area ceria may be used [161].

A similar analysis concerning possible risk of explosion during malfunctioning has to be done for physical mixtures of zeolite/NP and for activated carbon. As in the latter two cases higher surface area is accessible for adsorption, higher VOCs concentrations are expected if released suddenly. Additionally, as activated carbon itself is inflammable, this system needs special care. In order to build an intrinsic safe adsorber, dimensions and air flows should be chosen such that an explosive mixture can never be formed. However, all three strategies have a real potential for being used as in situ regenerable air purifier as the used material are low cost and readily available. Further improvements of regenerative air purifier are presented in the next chapter. As already existing buildings are difficult to refurbish with new air supply systems, a hypothetical implementation on future constructions is discussed.
6. Outlook

Scale up: As previously mentioned, the adaptation of established technologies such as the three-way-catalyst for domestic purposes, may indeed allow for a fast product development. As shown in chapter 4, the thermal regeneration of activated carbon and subsequent oxidation of released VOCs on a CeO$_2$/TiO$_2$ catalyst was successful. In order to test such a system on a larger scale, an activated carbon fixed bed and a three-way-catalyst may be assembled. Adsorption would happen at room temperature in an air flow. When regeneration is required, the catalyst is preheated. When the catalyst has reached working temperature, the AC fixed bed is heated as well. The desorbed VOCs are passed through the catalyst for total oxidation.

Formaldehyde: As formaldehyde is found in many indoor products and is suspected to be carcinogenic for humans, much attention for this particular VOC is required [162-164]. As AC has only little adsorption capacity towards such a small molecule, a substitute adsorber material is needed. Zeolites have shown to be suitable for this purpose. Adsorption of formaldehyde on a polar zeolite and subsequent desorption, followed by total oxidation over a catalyst, may represent a valuable solution for indoor formaldehyde elimination.

Extended adsorber: If we assume indoor air to contain formaldehyde, hydrocarbons (HC), halogenated- and acidic VOCs, then a combination of different adsorbers may be appropriate. Such an assembly may consist of the following components: AC, zeolite, AC/Al(III), oxidative catalyst and nanocrystalline metal oxide (see figure 6.1). On AC all large, low polar VOCs (e.g. $n$-decane) are adsorbed. Small polar molecules, such as formaldehyde or formic acid, are captured in the pores of polar zeolites. Halogenated VOCs, such as dichloromethane, are hold by Al(III) doped AC [165]. Regeneration is achieved thermally. During regeneration the released VOCs are oxidized over the catalyst. HC and small polar compounds are oxidized to CO$_2$ and water, whereas halogenated compounds are decomposed also to X$_2$ or acidic gases like H–X. These reactive products may be destructively adsorbed on nanocrystalline metal oxides such as Al$_2$O$_3$ or MgO [89, 90].
Figure 6.1: Possible assembly of an extended regenerable air filter. Air containing, hydrocarbons (HC), nonpolar VOCs, small halogenated VOCs and small polar VOCs (formaldehyde), is purified as follows: in a first AC filter all HC and nonpolar VOC are adsorbed. Small halogenated VOCs are captured on an AC filter doped with Al(III) salts. Finally, molecules like formaldehyde or formic acid are adsorbed on polar zeolites. During regeneration all these compounds are released and oxidized on an oxidative catalyst to CO₂, water and acidic gases like H-X (X = Cl). Acidic gases are finally destructively adsorbed on MgO and transformed to MgCl₂ [166]. Mg(OH)₂ is formed due to moisture, which can be transformed back to MgO by heating. As MgO is consumed, it has to be replaced periodically.

Integral approach: One of the main driving forces for this research is energy and maintenance saving. Hence, a more integrative solution is suggested, by tackling the problem much earlier in the casual chain. This includes for instance, VOCs mitigation by eliminating the sources. For instance, the use of furniture which does not emanate VOCs may help. The use of water based domestic products without volatile additives or the implementation of construction materials which do not produce emissions may also eliminate VOCs at the source. Indeed, such an approach seems utopian at the moment and may be it would remain as such for the near future.

However, novel architectural concepts more scope for low-energy and low-maintenance indoor air suply may be adapted. Hence, the here investigated regenerable air filters are implemented in a hypothetical future building. In the following case, outdoor air is assumed to be contaminated with particulate matter (PM) and different VOCs. Figure 6.2 displays a possible ventilation system for low-maintenance and low-energy demand. The figure represents a 4 story building (12 m edge) with a total volume assumed to be 1728 m³. The temperature is set to be 22 °C indoors and 27 °C outdoors (summer). At first, air is flushed into the building using a cyclone separator (a). Here, PM is removed from the air by cyclonic separation, where particles are separated according to gravity and inertial forces.
Figure 6.2: Hypothetical low-energy and low-maintenance clean air supply in a 4 story house. a) particulate matter is removed in a cyclone: no filter is required at this stage, very low maintenance; b) air is passive cooled by water evaporation: reduction of moisture, temperature regulation; c) VOCs are removed using in situ reg. air filters: regeneration allows thin filters, low pressure drop; d) warm polluted air from indoors rises to the roof: sun irradiation is exploited in summer, indoor air is heated by indoor activities and heating, natural convection; e) regeneration of filters: elimination of VOCs at high concentrations: reuse of filters, automated rotor exchanges filters.

No filters are needed and maintenance/cleaning can be done easily. The air contains now only VOCs and very fine dust. Before these APs are removed too, the air is cooled to indoor temperature via a passive water evaporation stage (b) as suggested by Rotzetter et al. [167]. At this stage some moisture is removed from the air. The cooling of 1728 m³ by 5 °C, to 22 °C requires the evaporation of less than 5 kg of water. After this point, the remaining APs are removed by in situ regenerable filters (c). As these filters can be easily regenerated, they do not need to be very thick. Hence, a low pressure drop is expected. The cleaned air is passed through the building and the single rooms. On the way, heat, APs, dust and excess moisture are transported away. The now warm air is passed through channels in the house front and transported to the roof (d). Additional, heat, originating from irradiation, helps to sustain this natural convection. On the roof, exhausted filters are reversely flushed with consumed air and regenerated at higher temperatures (e). The cycle can start again. The herein presented simple scheme of an air filtration circuit in intended to demonstrate a more integrative approach based on the investigated systems.
Appendix A: Supporting Information for Chapter 3

SA1: The corrected mass loss at 400 °C ($\Delta m_{400°C}$) is plotted against the adsorbed VOC in wet impregnation experiments. The compounds are listed in order of increasing boiling point. All tested materials (except CeO$_2$) were milled in water and calcined (1 h/500 °C in air) prior to testing.

SA2: The exothermic peaks in DTA analysis ($T_{exo}$) is plotted against the adsorbed VOC in wet impregnation experiments. The compounds are listed in order of increasing boiling point. All tested materials (except CeO$_2$) were milled in water and calcined (1 h/500 °C in air).
**SA3:** Relative mass loss (top left) and differential thermo analysis signal (bottom left) of diethylether adsorption on five different support materials. Ion current of reaction products (m/z = 18, 44, 2 and 31) evolving during sample heating (right block). All data were collected simultaneously.
Relative mass loss (top left) and differential thermo analysis signal (bottom left) of linalool adsorption on used support materials. Ion current of reaction products (m/z = 18, 44, 2 and 41) evolving during sample heating (right block). All data were collected simultaneously.
**SA5:** Relative mass loss (top left) and differential thermo analysis signal (top right) of limonene adsorption on used support materials. Ion current of reaction products (m/z = 18, 44, 2 and 68) evolving during sample heating (right block). All data were collected simultaneously.
SA6: Relative mass loss (top left) and differential thermo analysis signal (bottom left) of hexanoic acid adsorption on used support materials. Ion current of reaction products (m/z = 18, 44, 2 and 60) evolving during sample heating (right block). All data were collected simultaneously.
SA7: Relative mass loss (left) and differential thermo analysis signal (right) of triethylamine adsorption on used support materials. Ion current of reaction products (m/z = 18, 44, 2 and 58) evolving during sample heating (right block). All data were collected simultaneously.
Relative mass loss (left) and differential thermo analysis signal (right) of blanks of five different support materials.

Table SA 1 Relative mass loss at 400 °C wet impregnation (raw data)

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<th>Blank</th>
<th>Diethylether</th>
<th>Linalool</th>
<th>Limonene</th>
<th>Hexanoic acid</th>
<th>Triethylamine</th>
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<td>2.5</td>
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<td>4</td>
<td>7.2</td>
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<td>5.7</td>
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<td>H-ZSM-5</td>
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<td>15.8</td>
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SA9: Left: Relative mass loss of wet impregnated adsorber materials with different compounds dissolved in diethylether. Right: Exothermic event temperature of adsorbates on different support materials from exothermic peak (DTA) was taken as an indicator for reaction. Additionally CO$_2$ evolution is plotted. Contributions originating from dietylether (solvent) in samples containing linalool, limonene, hexanoic acid and triethylamine were neglected.
Table SA 2 Wet impregnation adsorption data

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<th>$T_{exo}$ [°C]</th>
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<td>280</td>
</tr>
<tr>
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<td></td>
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<td>180-250/380</td>
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<td>$\text{CeO}_2/\text{13X calc.}$</td>
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<td>$\text{13X calc.}$</td>
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<tr>
<td>$\text{13X calc.}$</td>
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<td>300</td>
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<td>$\text{CeO}_2/\text{13X calc.}$</td>
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<td>$\text{13X calc.}$</td>
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<td>$\text{13X calc.}$</td>
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*blank and diethylether subtracted*
Table SA 3 Gas phase adsorption data

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<td>265</td>
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<td>13X calc.</td>
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<td>180</td>
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<tr>
<td>CeO₂/H-ZSM-5 calc.</td>
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<td>265</td>
</tr>
<tr>
<td>H-ZSM-5 calc.</td>
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<td>270</td>
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<td>CeO₂/13X calc.</td>
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<td>195/255</td>
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<td>200</td>
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<td><strong>Triethylamine</strong></td>
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<td>CeO₂</td>
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<td>175/230</td>
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<tr>
<td>CeO₂/H-ZSM-5 calc.</td>
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<tr>
<td>H-ZSM-5 calc.</td>
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<td>CeO₂/13X calc.</td>
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<tr>
<td>13X calc.</td>
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<td>290/340</td>
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* blank subtracted
SA10: STEM micrographs of CeO$_2$/H-ZSM-5 (a) and H-ZSM-5 (b) after milling and calcination. EDX mapping region (c) and elemental analysis for cerium (e), oxygen (d) and aluminum (f) of cerium oxide dispersion on H-ZSM-5.

SA11: STEM micrographs of CeO$_2$/13X (a) and 13X (b). EDX mapping region of CeO$_2$/13X (c), oxygen (d) and aluminum (f) dispersion on 13X.
SA12: TEM micrographs of CeO$_2$/H-ZSM-5 (left) and CeO$_2$/13X (right).

SA13: EDX mapping of CeO$_2$/13X calcined (cyan = Ce, magenta = Si, yellow = aluminum)
**SA14:** XRD pattern of here used materials

**SA15:** Comparison of gas phase adsorption, external surface and pore volume
SA Cost estimation

A detailed economic study was not performed. However, assuming an average concentration of indoors VOC of 0.5 ppm (equals 2.6 mg/m$^3$ for an average molecular weight of 130 g/mol) (Huey-Jen Su, Atmospheric Environment 41 (2007) 1230–1236) and an adsorption capacity of 3 wt. %, this would correspond to 30 g VOC/kg adsorber. For an average room volume of 50 m$^3$ (total VOC about 130 mg) this would correspond to about 230 room volumes (230 r. V./kg adsorber). At this point the adsorber needs to be regenerated. Systems based on activated carbon can adsorb about 10 wt. % (100 g VOC) corresponding to about 770 r. V./kg adsorber. However, at this point the activated carbon must be replaced or regenerated separately, as regeneration on place would simply release the captured VOC in the environment. This will increment significantly the maintenance costs and the carbon emissions as small amounts of AC are not reactivated but incinerated. Compared to HVAC systems where the indoor air is replaced typically three times per hour large air volumes must be filtered, cooled or heated in order to assure good indoor air quality. This will further increment the running costs. Additionally, an HVAC system is a complex construction and periodical maintenance is required.

| Table SA4 Cost estimate for weekly regeneration (2.2 kg adsorber) |
|-------------------------|-----------------|-----------------|-----------------|-----------------|
| Material               | Material price  | Adsorber material costs | Time to exhaustion | Cost for one year of operation |
|                        | [$/kg]          | [$/Adsorber]       | [d]              | [$]              |
| CeO$_2$/zeolite        | 20              | 44               | 7               | 144 $^a$         |
| Activated carbon       | 2               | 4.4              | 23              | 816 $^b$         |

$^a$ assuming 2 service/maintenance  
$^b$ assuming 15 service/exchange plus material  
$^c$ air exchange is 3 room volumes per hour  
Service/maintenance costs: 50$/service

From the table above is visible, that after about 3 cycles (exhaustion/regeneration for CeO$_2$/zeolite) the acquisition costs are equalized.
## Appendix B: Supporting Information for Chapter 4

### Table SB1: Mass balance of adsorption and desorption cycles

#### Triethylamine

<table>
<thead>
<tr>
<th>AC 500 mg</th>
<th>Cycle</th>
<th>Total weight [g]</th>
<th>Load [g]</th>
<th>Reg. [g]</th>
<th>AC Loss [mg]</th>
<th>AC Loss [%]</th>
<th>Ads. Cap. [%]</th>
<th>Recovery [mg]</th>
<th>Recovery [%]</th>
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#### n-Decane

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<th>Total weight [g]</th>
<th>Load [g]</th>
<th>Reg. [g]</th>
<th>AC Loss [mg]</th>
<th>AC Loss [%]</th>
<th>Ads. Cap. [%]</th>
<th>Recovery [mg]</th>
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#### Limonene

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<th>AC Loss [mg]</th>
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**Figure SB1**: Additional masses found for limonene during desorption.

**Figure SB2**: Desorption and combustion cycles for \(n\)-decane and TEA.

**Figure SB3**: Mass balance of adsorption and regeneration cycles for TEA, \(n\)-decane and limonene on AP4-60 granules (200 – 400 μm). Left: VOC adsorption capacity, right: AC mass loss after each cycle.
Figure SB4: Hg intrusion porosimetry of starting material.
References


