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Research Article

Carbon Dioxide Capture from Ambient Air Using Amine-Grafted Mesoporous Adsorbents

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Anthropogenic emissions of carbon dioxide (CO_2) have been identified as a major contributor to climate change. An attractive approach to tackle the increasing levels of CO_2 in the atmosphere is direct extraction via absorption of CO_2 from ambient air, to be subsequently desorbed and processed under controlled conditions. The feasibility of this approach depends on the sorbent material that should combine a long lifetime with nontoxicity, high selectivity for CO_2, and favorable thermodynamic cycling properties. Adsorbents based on pore-expanded mesoporous silica grafted with amines have previously been found to combine high CO_2 adsorption capacity at low partial pressures with operational stability under highly defined laboratory conditions. Here we examine the real potential and functionality of these materials by using more realistic conditions using both pure CO_2, synthetic air, and, most importantly, ambient air. Through a combination of thermogravimetric analysis and Fourier transform infrared (TGA-FTIR) spectroscopy we address the primary functionality and by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy the observed degradation of the material on a molecular level.

1. Introduction

Anthropogenic emissions of carbon dioxide (CO_2) have attracted worldwide attention, since they are considered as the main contributor to climate change. Severe constraints on emission rates, however, could hinder economic growth, especially in developing countries [1, 2]. Even an issue of The Economist has been devoted to these issues: "Welcome to the Anthropocene" [3].

The number of different approaches suggested to tackle this problem is increasing rapidly [4]. Flue gases emitted from large point sources such as electricity generating power plants or cement factories are the focus of processes related to carbon capture and sequestration (CCS). CCS aims to capture the carbon dioxide directly at the emission sources and bury it in underground storages such as depleted oil and gas reservoirs. State-of-the-art approaches for the capturing stage of CCS apply mainly amine-based aqueous solutions as monoethanolamine (MEA) or diethanolamine (DEA) [5, 6]. Such liquid amines, however, are subject to a number of serious drawbacks; most notably a part of these toxic compounds will be lost into the atmosphere by evaporation, and the remainder will gradually degrade by oxidative processes [5, 6].

Obviously, on-site capture of CO_2 at large point sources can be conducted more cost-effectively than the capture from small and mobile sources like vehicles powered by carbonaceous fuels [1, 7, 8]. However, the elimination of emissions from power plants alone is not sufficient to stabilize the current CO_2 levels in the atmosphere [2]. Therefore, also other additional feasible alternatives must be addressed. One such approach is to locally and directly extract CO_2 from ambient air passing over absorber surfaces [1, 9]. The absorbed CO_2 should preferably be desorbed and processed further under controlled conditions, creating useful materials or fuels and so forth. This concept eliminates the necessity for pipelines or any equivalent systems to transport the captured CO_2 to sites for CCS.

The key and prime factor determining the feasibility of this approach is to find a suitable sorbent functioning under ambient air conditions for numerous adsorption and desorption cycles [1]. Any suitable candidate must also be nontoxic and environmentally benign to produce and use. Further desirable properties are long-term stability and high selectivity for CO_2 [10]. In addition, the ideal sorbent should possess favorable thermodynamic properties to enable rapid cycling and to avoid excessive energy consumption.

There are basically 2 physical processes applicable for CO_2 capturing. Absorption is a bulk phenomenon occurring throughout the body of the sorbent material, whereas the CO_2 uptake process is adsorption if the molecules are attracted and retained on the surface. At medium or high CO_2 partial pressures, absorption of CO_2, as for example practiced with amine solutions, is applicable. For physical adsorbents such as carbon-based materials and metal-organic frameworks (MOFs), CO_2 uptake capacity is strongly pressure dependent and thus low at low partial pressures. In contrast to this, high-surface solid materials loaded with amine-containing molecules are capable of both chemical and physical adsorption. At low CO_2 concentrations, as encountered in ambient air (≈390 ppm), the adsorption on functionalized mesoporous supports is chemical, whereas physical adsorption within the pores occurs at higher partial pressure [11].

The hydroxides, oxides, and carbonates of Na and Ca have been well known as CO_2 absorbents for many decades [12, 13]. The regeneration of these compounds, however, requires high temperatures and is therefore neither cost nor energy effective [9]. Therefore, the probably most frequently applied solid materials are activated carbons and zeolites. However, CO_2 adsorption capacity of activated carbons is rather low, whereas in the case of zeolites, selectivity towards CO_2 is drastically affected by humid conditions, that is, the presence of water vapor [10]. Thus, zeolites are only applicable for CO_2 adsorption if the water vapor is removed prior to the adsorption step [14–16].

In contrast to the case of zeolites, the amount of CO_2 absorption by amines is known to be unaffected or even increased under humid conditions. This is usually claimed to be due to the additional formation of bicarbonate besides the main reaction of carbamate formation [17, 18]. The concept of combining the well-known absorption characteristics of liquid amines with solid supports characterized by high-surface areas has been studied by many research groups [19–21]. Adsorbents of this kind often consist of a supporting matrix of mesoporous silica loaded with amine-containing molecules, either just physically or more elaborately chemically by grafting [9, 22]. Examples of this adsorbent type are 3-aminopropyl-triethoxysilane grafted on mesoporous MCM-48 silica [21], hyperbranched aminosilica (HAS) supported on SBA-15 [9], and pore-expanded mesoporous silica (PE-MCM-41) grafted with aminosilanes [10, 23–25]. For grafted PE-MCM-41 the thermal stability of both the mesoporous pore-expanded supporting matrix as well as of the amine-containing components has been vividly investigated [11, 15, 19, 26, 27]. TGA experiments have shown that the PE-MCM-41 matrix itself is thermally stable up to 1000°C, whereas the decomposition of the grafted amine groups starts already at 200–250°C [24, 26, 28].

Numerous studies have shown that such specially developed CO_2 sorbents indeed can combine high CO_2 adsorption capacities at low partial pressures with favorably low regeneration temperatures and furthermore operational stability under well-defined laboratory conditions [10, 23, 24]. Experiments conducted on these types of materials, with no chemical conversion involved, under more realistic conditions, however, have been very few; examples are individual adsorption tests using air [29] or carbon-free (CF) air in the laboratory [25, 30]. Thus, to ensure and verify, or even dismiss, functionality in practice, there is an urge to investigate the stability of these materials in real air and with realistic adsorption and desorption cycles.

Therefore we here, for the first time, investigate in detail the adsorption of CO_2 from ambient air in an applied study with admittedly less-controlled conditions—but more relevant from application perspective. The materials used are based on mesoporous silica grafted with amines and the technique for adsorbent regeneration thermal swing adsorption (TSA), that is, heating and cooling cycles. In more detail, triamine- and aminopropyl-grafted PE-MCM-41 mesoporous silica (TRI-PE-MCM-41 and MONO-PE-MCM-41) were selected as these materials have been reported to combine high CO_2 adsorption capacity with stable operation during 700 cycles of CO_2 adsorption and desorption in humid gases [10]. To enhance our possibilities of proper interpretation, adsorption experiments in pure CO_2 were primarily conducted, followed by laboratory studies using synthetic air containing 400 ppm CO_2, and, finally, a selected adsorbent material was tested under real varying conditions in ambient air and by applying different desorption parameters. To the best of our knowledge, this is the first study to properly analyze these types of CO_2 adsorbent materials, based on only weak physical adsorption to a solid matrix compound grafted with adsorbent sites, performance, and stability in ambient air.

2. Materials and Methods

2.1. CO_2 Adsorbent Materials. Two adsorbent materials both consisting of a matrix of mesoporous PE-MCM-41 silica with amine functionalized surfaces were used [10]. The amines were incorporated by grafting with 3-(aminopropyl)-trimethoxysilane for MONO-PE-MCM-41 (MONO) and 2-[2-(3-trimethoxy-silyl-propyl-amino)ethylamino]ethylamine for TRI-PE-MCM-41 (TRI), respectively. The acronyms MONO and TRI will henceforth be used for the two absorbent materials. The total loading of amines is 4.3 mmol/g for MONO (primary amines) and 7.9 mmol/g for TRI (primary and secondary amines). As an example of the porosity of the materials the pore size of TRI is 9.4 nm [31], while both the detailed preparation procedures and structural characteristics of the materials are to be found in the original papers [10, 11, 28, 31].

2.2. Gases. Scientific grade gases provided by AGA Gas AB were used for all experiments, that is, pure CO_2, pure N_2, and synthetic air consisting of N_2 containing 20.9% O_2 and 400 ppm CO_2. A humid gas flow was produced by passing dry gas through an isolated humidifier bottle filled with ultrapure water ("Milli-Q") held at a constant temperature. The level of moisture in the gas stream corresponds to the equilibrium vapor pressure at the temperature in the humidifier bottle, set to 30°C. This resulted in a relative humidity of 0.45% for desorption in humid gases at 100°C and a relative humidity of 3% for desorption in humid air at 75°C (Table 1).

2.3. Experimental

2.3.1. TGA-FTIR. For the adsorption and desorption experiments thermogravimetric analysis (TGA) (with a temperature ramp of 50 K/min) was performed using a TG 209 F1 Iris equipment (Netzsch). The TGA equipment was connected to a Fourier transform infrared (FTIR) spectrometer, Vector 22 (Bruker), via a heated and temperature-controlled transfer line, together creating a combined TGA-FTIR set-up for spectroscopic analysis of the evolved gases from the TGA. Using ZnSe windows and a gas cell (6 mm L × 1.8 mm Ø), this was calibrated for quantitative analysis of CO_2 by heating known amounts of $NaHCO_3$ to release defined masses of CO_2 (and H_2O under transformation to Na_2CO_3). All CO_2 quantification was performed using the FTIR software package OPUS 6.5 and integration limits in the spectra set to 2208–2451 cm^{-1}.

2.3.2. FTIR (DRIFT). FTIR analysis in diffuse reflectance infrared Fourier transform (DRIFT) geometry was performed using an IFS 66v/S spectrometer (Bruker) equipped with a diffuse reflection unit (Selector/Specac). The mid-IR spectra (660–5700 cm^{-1}) were recorded using a KBr beam splitter and an MCT detector. Since the real adsorption spectra cannot be collected in DRIFT mode, the logarithm of the inverse reflection spectra was used and is reported. For the measurements *ca* 3 mg of sample was ground together with *ca* 480 mg KBr in an agate mortar, and a common background of KBr was employed.

2.3.3. Experimental Parameters. Due to the different materials and gases used and the different conditions applied, as well as the more applied nature of the study, the matrix of parameters used for the adsorption and desorption experiments becomes complex. All detailed information on experimental settings: gas, gas flow, temperature range, times, relative humidity, and so forth during adsorption and desorption are therefore compiled separately in Table 1. Some further details are also given in the relevant parts of the Results and Discussion section.

3. Results and Discussion

To verify the performance and stability of our experimental set-up and experiments at large the reproducibility was first compared with the existing literature using well-defined laboratory conditions and cycling our absorbent materials in pure CO_2. Subsequently, as a slightly more complex stage, adsorption experiments were conducted in synthetic air, both dry and humidified, likewise under controlled laboratory conditions. In the next stage and the major and innovative part of our study, the adsorbents were tested using ambient air under real atmospheric conditions. Finally, due to the observed phenomena of rapid material degradation during this latter stage, special efforts were made, including designated spectroscopic analysis, to identify and discuss how to mitigate the parameters and main mechanisms hindering the practical application of this kind of CO_2 adsorption and desorption materials.

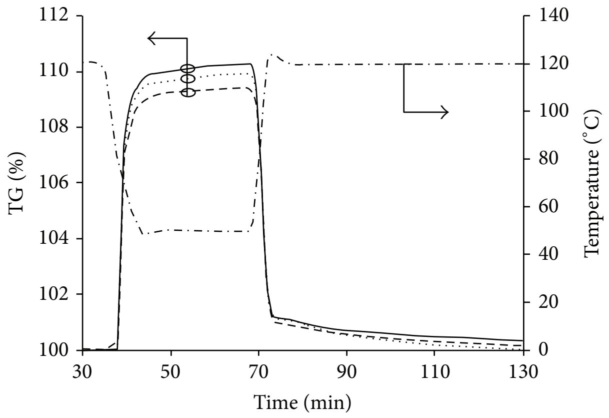

FIGURE 1: 3 individual 1st TGA traces with pure CO_2 as gas and TRI as absorbent as function of time and temperature. All experimental details are listed in Table 1.

3.1. Pure CO_2-Based Experiments. As outlined above, the accuracy and reproducibility of our experimental set-up was first investigated by comparing with literature results, using pure CO_2 as the probing gas [10]. In Figure 1 this is exemplified by the TGA traces for 3 separate and individual 1st adsorption/desorption cycles using TRI as the adsorbent material. After the common activation step, heating to 120°C for 40 min, all the individual experiments in Figure 1 render the 1st cycle with approximately 10 wt.% CO_2 adsorption, which is in excellent agreement with the literature [10], and also the reproducibility of the adsorption/desorption profiles is reassuring.

With the reproducibility of the results gained for the 1st cycles at hand, the most important issue is of course the behavior upon repeated adsorption/desorption. Here both the MONO and TRI adsorbents showed a pronounced decrease in adsorption capacity already after 10 cycles, from approx. 10 and 9 wt.%, respectively, down to approximately 8.5 and 6 wt.% (Figure 2). This is in stark contrast to prior studies that have revealed only a slight deterioration in the CO_2 adsorption capacity, even after 40 cycles [10].

We can only speculate on the reason for the observed discrepancy; while our experiments in general were conducted under the exact same conditions as described in Sayari et al., the duration of the desorption time was not revealed. Thus our chosen desorption time of 60 min (at 120°C) might very well be longer. Our choice of an extended desorption time is indeed a way to simulate an increased number of regeneration

Table 1: Experimental settings, gas, gas flow, temperature range, times, relative humidity, and so forth during adsorption and desorption.

Experiment	Figure(s)	Material(s)	Adsorption					Desorption				
			Gas	Flow (mL/min)	Temperature (°C)	Time	RH (%)	Gas	Flow (mL/min)	Temperature (°C)	Time (min)	RH (%)
10 TGA cycles, dry	1, 2, 4	MONO, TRI	CO_2	50	50	30 min	0	N_2	50	120[1]	60	0
3 cycles outdoor adsorption	3, 4	TRI	Air	—	(+5)–(−5)	Overnight	60–80	Synthetic air	10	100	120	0.45
3 cycles outdoor adsorption	3	TRI	Air	—	(0)–(−5)	Overnight	90–100	Synthetic air	10	75	120	3
3 cycles outdoor adsorption	3	TRI	Air	—	(0)–(−2)	Overnight	90–100	N_2	10	100	120	0.45
4 TGA cycles, humid	3	TRI	Synthetic air	10	30	180 min	73	Synthetic air	10	100	15	0.45
4 TGA cycles, dry	3	TRI	Synthetic air	10	30	180 min	0	Synthetic air	10	100	15	0
Atmospheric trace gases	—	TRI	Air	—	(0)–(−10)	35 h	90	Synthetic air	10	100	120	0.45
Atmospheric trace gases	—	MONO, TRI	Air	—	(+10)–(+20)	41 h	40–80	Synthetic air	10	100	120	0.45
Atmospheric trace gases	—	TRI	Air	—	(0)–(−10)	191 h	80–100	Synthetic air	10	100	120	0.45
Atmospheric trace gases	5	MONO, TRI	Air	—	(0)–(+20)	202 h	30–90	Synthetic air	10	100	120	0.45
Atmospheric trace gases	5	MONO, TRI	Air	—	(0)–(+20)	514 h	30–70	Synthetic air	10	100	120	0.45

[1] Temperature ramp: 20 K/min.

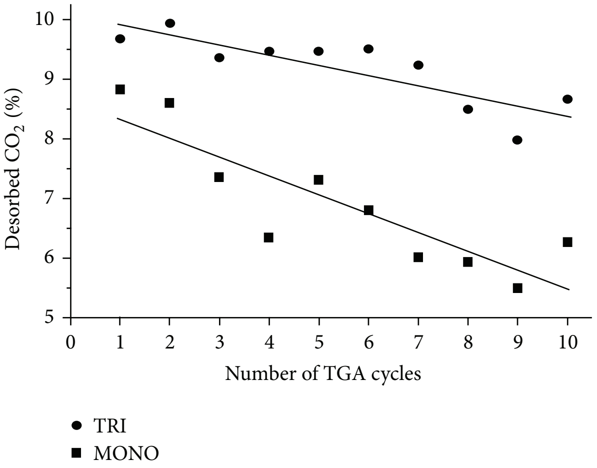

FIGURE 2: Amount of CO_2 desorbed from MONO and TRI, respectively, as functions of the number of TGA adsorption/desorption cycles. Lines are only guides to the eye. All experimental details listed in Table 1.

cycles, using the notion of faster reaction rates at the highest temperature of the cycle.

Turning back to the 1st cycle data presented in Figure 2, the initial adsorption capacities for MONO and TRI were 8.8 wt.% and 9.7 wt.%, respectively, both in agreement with the literature [10, 26]. The only slightly lower capacity of MONO was expected as it is directly related to the surface density and not the total loading (being only *ca* half of that of TRI) of amine groups [26]. As the overall data compiled in Figure 2 also indicate a slightly faster degradation of MONO, TRI will be more extensively studied in the following.

3.2. Synthetic Air-Based Experiments. The use of synthetic air, both dry and humidified, adds complexity to the adsorption process(es). The influence on the CO_2 adsorption characteristics by any humidity present has been extensively studied for amine-functionalized solid materials [10, 17, 23, 29, 30]. In the absence of any humidity, CO_2 is known to react with the amine groups to form carbamate (reaction (1) below), whereas in the presence of humidity, the formation of bicarbonate is competing (reaction (2) below):

$$2RNH_2 + CO_2 \Longleftrightarrow RNHCO_2^{-}NH_3R^{+} \quad (1)$$

$$RNH_2 + CO_2 + H_2O \Longleftrightarrow RNH_3^{+}HCO_3^{-} \quad (2)$$

As seen in (1), two amine groups may react with one CO_2 molecule to form carbamate, whereas in (2), only one amine group is needed to bind one CO_2 molecule. The two reactions are competitive, but the dry process of carbamate production (1) is kinetically favored [23, 24]. Therefore, a lower adsorption of CO_2 from humid air, as can be found in Figure 3 where the TGA desorption data for cycles 2 and 3 show approximately 2.8 wt.% for dry and 2.4 wt.% for humidified air, respectively, may be attributed to slower kinetics. These data indirectly also suggest that the adsorbent material is slightly more stable in humid air, giving further support to water vapor having a positive effect on the stability of the grafted amine groups by inhibiting urea formation [10]. The latter will be further commented on in Section 3.4.

3.3. Experiments Using Ambient Air and Real Atmospheric Conditions. So far, the investigated adsorption materials have shown both promising capacities and reasonable cyclabilities, as previously noted in the literature [10, 11, 19, 24, 25, 27]. The most crucial test, however, is performance under real atmospheric (i.e., outdoor) conditions—a concise "reality check." It is useful to note that while the adsorption process may involve various species when real outdoor air is used, our set-up can unambiguously quantify the evolved (desorbed) CO_2 accurately.

In Figure 3 outdoor exposure is encouragingly found to outperform the laboratory tests for the 1st cycle. The explanation for this is, however, mainly two-fold; first, in the indoor laboratory experiments, a higher adsorption temperature had to be used compared to the outdoor experiments (winter conditions). Second, a longer adsorption time was applied in the outdoor compared to the indoor experiments. The latter were limited to 3 hours for practical reasons. Hence, we cannot possibly claim any physical or chemical reason for a better overall performance, and this is also not to be expected. In addition, a fast decrease in the 2nd cycle from 5.1 to 1.2 wt.% CO_2 desorbed is observed (Figure 3). Already in the 3rd cycle the CO_2 amount is below the FT-IR detection limit.

However, many routes can be explored to reduce this drastic decrease. Our first approach was to use a lower desorption temperature; 75°C has previously been found to be sufficient under laboratory conditions [19, 31]. However, the initial amount of desorbed CO_2 was reduced to only 0.5 wt.% (Figure 3). Subsequently, the 2nd and 3rd cycles resulted in only 0.1 wt.% CO_2. Thus a desorption temperature of 75°C is in practice too low when applied to outdoor exposed samples.

A second approach is based on that the stability of liquid amine-based absorbents, often used in flue gas applications, has been shown to be affected by the presence of oxygen, leading to the formation of heat stable salts at temperatures above 80°C [32, 33]. However, our desorption in pure humid N_2, rather than synthetic air, did not significantly improve the TRI adsorbent stability (Figure 3).

3.4. Identification of Parameters and Main Mechanisms Affecting Materials Degradation. In order to rationally improve our absorbent materials the understanding of the underlying reasons for the observed degradation needs to be improved. Therefore, several especially designed experiments were undertaken.

First, assuming that loss of capacity is primarily due to simple degradation of the amine groups, these were characterized using FTIR spectroscopy in a DRIFT set-up. In Figure 4 the FTIR (DRIFT) spectra recorded for pristine, noncycled TRI as well as after outdoor exposure and cycling are shown. Notable differences are observable in the NH_2 deformation band at ~1600 cm^{-1}, a band associated with the presence of primary amine groups. This band decreases as a function of cycles, strongly suggesting that the loss in CO_2 adsorption capacity is connected with a loss of primary amine groups. In addition, spectral differences in the spectra are also

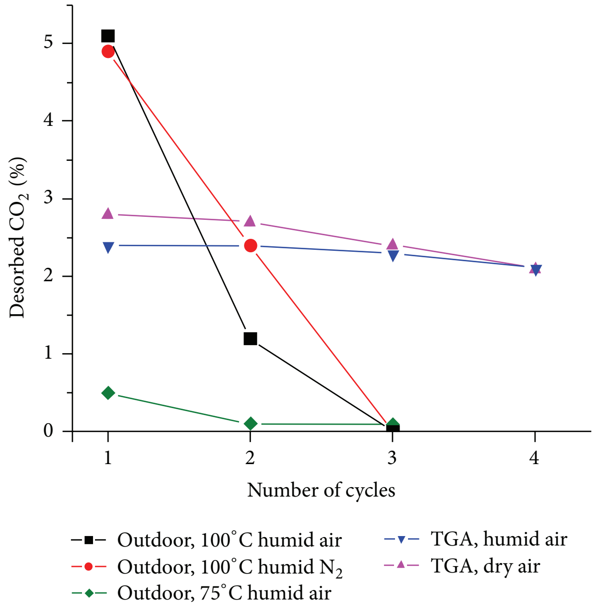

Figure 3: Amount of CO_2 desorbed from TRI as functions of adsorption and desorption conditions and the number of cycles. Lines are only guides to the eye. All experimental details are listed in Table 1.

found at ~1660 cm^{-1}, a band indicative of formation of urea groups [10, 17, 27, 34]. As this band has the opposite evolution, the observed degradation is also related to the formation of urea groups. In addition, a small shoulder at *ca* 1490 cm^{-1} appears in Figure 4(c), possibly also related to urea formation. However, this shoulder might even be hidden within the main peak at 1450 cm^{-1} in the spectrum of fresh TRI (Figure 4(a)). The degradation observed for all samples undergoing thermal desorption is also supported by the literature observations of rapid decreases in adsorption capacity due to the formation of urea linkages at the expense of amine groups [35].

Second, since the basic reactions of TRI are similar to those of liquid amines [23], it is natural to investigate whether comparable degradation processes as for these might occur when exposed to the atmosphere. In detail, liquid amines react with sulfur-containing gases in the atmosphere such as carbonyl sulfide (COS), carbon disulfide (CS_2), and sulfur dioxide (SO_2) to form various heat stable salts such as oxalates, formates, thiosulfates and acetates [36]. Letting pure SO_2 act on TRI caused an irreversible CO_2 adsorption capacity decrease from 6.9 to 3.9 wt.% [34]. Indeed, DRIFT spectra revealed the disappearance of the significant primary amine band at ~1600 cm^{-1} [28]. However, atmospheric SO_2 cannot possibly explain the main part of our observed rapid degradation, since the SO_2 concentration in [34] exceeded the 3 μg m^{-3} found in Göteborg air [37] by a factor of 10^5.

Third, longer outdoor exposures, 35 to 514 hours, without any regenerative cycling were made (Table 1). While there are some variations in the amount of desorbed CO_2, in the range from 3.1 to 7.8 wt.% (not shown) depending on the varying conditions, the degradation found upon cycling (Figure 3) cannot be ascribed to reactions with atmospheric trace gases;

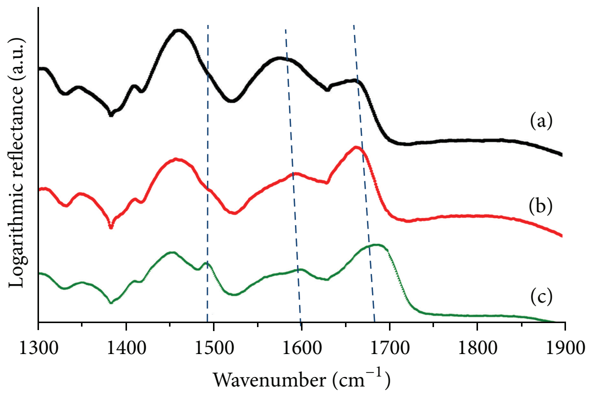

Figure 4: FTIR (DRIFT) spectra in the region 1300–1900 cm^{-1} of the TRI adsorbent material as functions of adsorption and desorption conditions and the number of cycles: (a) fresh, (b) outdoor, 100°C humid air, 3 cycles, and (c) TGA, 120°C dry air, 10 cycles. Further experimental details listed in Table 1. The band at ~1660–1670 cm^{-1} and the shoulder at ~1490 cm^{-1} are both assigned to urea groups and the band at 1600 cm^{-1} to NH_2.

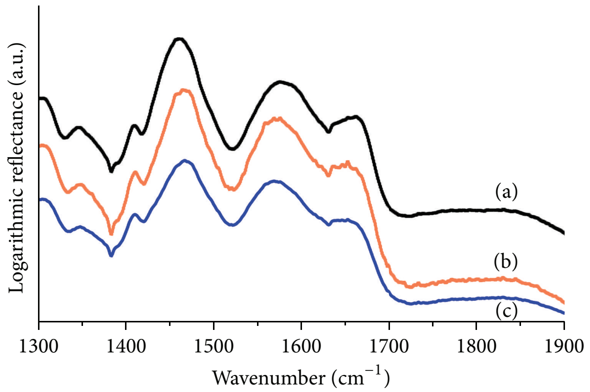

Figure 5: FTIR (DRIFT) spectra in the region 1300–1900 cm^{-1} of the TRI adsorbent material as a function of long-time outdoor exposure: (a) fresh, (b) outdoor 202 h, and (c) outdoor 514 h. Further experimental details listed in Table 1. The band at ~1660 cm^{-1} is assigned to urea groups and the band at ~1600 cm^{-1} to NH_2.

the urea band at 1660 cm^{-1} and the NH_2 band at 1600 cm^{-1} in the DRIFT spectra are both largely unchanged even after 514 hours (Figure 5). Thus, material degradation due to reaction with atmospheric trace gases, without any cycling, seems negligible.

Finally, the considerably longer thermal desorption times used may have a deleterious effect on the adsorption capacity. Degradation of amine-based absorbents as a consequence of thermal desorption was postulated by Drage et al. [17], suggesting two reaction mechanisms (albeit for slightly different adsorbents):

$$R_2NH_2{}^+ + R_2NCO_2{}^- \Longleftrightarrow R_2NCONR_2 + H_2O \tag{3}$$

$$2R_2NH + CO_2 \Longleftrightarrow R_2NCONR_2 + H_2O \tag{4}$$

Urea is either formed in a secondary reaction of the carbamate ion (3) or by the direct reaction of CO_2 with the amine groups of the adsorbent (4). The set-up by Drage et al. used temperatures above 130°C [17]; we used 100°C, and previously cycling of TRI in dry gases caused urea formation even at 70°C (albeit at a much slower rate) [10]. In the latter study, water vapor was shown to stabilize the amine groups by inhibiting the urea formation. In stark contrast, our outdoor exposure experiments showed a clear degradation upon cycling, despite the presence of water—as verified by the DRIFT spectra. In all, a reduced CO_2 adsorption capacity due to degradation by urea formation seems to be an inherent fate for this kind of absorbent, although the rate might be controlled by parameters as humidity, temperature, and duration of the thermal desorption stage.

4. Conclusions

By using pure CO_2, synthetic air, and finally real atmospheric conditions, the adsorbent materials used were found to have excellent initial CO_2 adsorption capacities, but upon exposure to real atmosphere conditions and with more realistic adsorption/desorption times, degradation becomes an issue. Reactions with atmospheric trace gases or with atmospheric oxygen are both negligible, but due to the formation of urea groups for all samples undergoing thermal desorption, a rapid decrease in adsorption capacity is a general problem. The advanced spectroscopic set-ups used (TGA-FTIR, DRIFT) and the results thereby obtained stress the strength of combining detailed molecular level analysis with realistic conditions for the application to be monitored.

Conflict of Interests

The authors declare that there is no conflict of interests, for example, financial, for any of the authors with respect to the work presented.

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References

[1] K. S. Lackner, P. Grimes, and H.-J. Ziock, "*Capturing Carbon Dioxide From Air*," 2013, http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/7b1.pdf.

[2] J. T. Houghton and Intergovernmental Panel on Climate Change Working Group III, Eds., *Climate Change 1994*, Cambridge University Press, Cambridge, UK, 1995.

[3] The Economist, "Welcome to the Anthropocene, 26 May 2011," 2013.

[4] K. B. Lee, M. G. Beaver, H. S. Caram, and S. Sircar, "Reversible chemisorbents for carbon dioxide and their potential applications," *Industrial and Engineering Chemistry Research*, vol. 47, no. 21, pp. 8048–8062, 2008.

[5] D. M. D'Alessandro, B. Smit, and J. R. Long, "Carbon dioxide capture: prospects for new materials," *Angewandte Chemie*, vol. 49, no. 35, pp. 6058–6082, 2010.

[6] J. Oexmann, A. Kather, S. Linnenberg, and U. Liebenthal, "Post-combustion CO_2 capture: chemical absorption processes in coal-fired steam power plants," *Greenhouse Gases*, vol. 2, no. 2, pp. 80–98, 2012.

[7] R. Socolow and M. Desmond, "*Direct air capture of CO_2 with chemicals*, A Technology Assessment for the APS Panel on Public Affairs," 2011, http://www.aps.org/policy/reports/assessments/upload/dac2011.pdf.

[8] K. Z. House, A. C. Baclig, M. Ranjan, E. A. van Nierop, J. Wilcox, and H. J. Herzog, "Economic and energetic analysis of capturing CO_2 from ambient air," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 108, no. 51, pp. 20428–20433, 2011.

[9] S. Choi, J. H. Drese, P. M. Eisenberger, and C. W. Jones, "Application of amine-tethered solid sorbents for direct CO_2 dapture from the ambient air," *Environmental Science & Technology*, vol. 45, no. 6, pp. 2420–2427, 2011.

[10] A. Sayari and Y. Belmabhout, "Stabilization of amine-containing CO_2 adsorbents: dramatic effect of water vapor," *Journal of the American Chemical Society*, vol. 132, no. 18, pp. 6312–6314, 2010.

[11] Y. Belmabkhout and A. Sayari, "Effect of pore expansion and amine functionalization of mesoporous silica on CO_2 adsorption over a wide range of conditions," *Adsorption*, vol. 15, no. 3, pp. 318–328, 2009.

[12] V. Nikulshina, N. Ayesa, M. E. Gálvez, and A. Steinfeld, "Feasibility of Na-based thermochemical cycles for the capture of CO_2 from air-Thermodynamic and thermogravimetric analyses," *Chemical Engineering Journal*, vol. 140, no. 1–3, pp. 62–70, 2008.

[13] V. Nikulshina, C. Gebald, and A. Steinfeld, "CO_2 capture from atmospheric air via consecutive CaO-carbonation and CaCO3-calcination cycles in a fluidized-bed solar reactor," *Chemical Engineering Journal*, vol. 146, no. 2, pp. 244–248, 2009.

[14] F. Brandani and D. M. Ruthven, "The effect of water on the adsorption of CO_2 and C 3H8 on type X zeolites," *Industrial and Engineering Chemistry Research*, vol. 43, no. 26, pp. 8339–8344, 2004.

[15] R. Serna-Guerrero, Y. Belmabkhkout, and A. Sayari, "Influence of regeneration conditions on the cyclic performance of amine-grafted mesoporous silica for CO_2 capture: an experimental and statistical study," *Chemical Engineering Science*, vol. 65, no. 14, pp. 4166–4172, 2010.

[16] J. C. Santos, F. D. Magalhaes, and A. Mendes, "Contamination of zeolites used in oxygen production by PSA: effects of water and carbon dioxide," *Industrial & Engineering Chemistry Research*, vol. 47, no. 16, pp. 6197–6203, 2008.

[17] T. C. Drage, A. Arenillas, K. M. Smith, and C. E. Snape, "Thermal stability of polyethylenimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies," *Microporous and Mesoporous Materials*, vol. 116, no. 1–3, pp. 504–512, 2008.

[18] C. Chen, S.-T. Yang, W. S. Ahn, and R. Ryoo, "Amine-impregnated silica monolith with a hierarchical pore structure: enhancement of CO_2 capture capacity," *Chemical Communications*, no. 24, pp. 3627–3629, 2009.

[19] R. S. Franchi, P. J. E. Harlick, and A. Sayari, "Applications of pore-expanded mesoporous silica. 2. Development of a high-capacity, water-tolerant adsorbent for CO_2," *Industrial and Engineering Chemistry Research*, vol. 44, no. 21, pp. 8007–8013, 2005.

[20] S. Satyapal, T. Filburn, J. Trela, and J. Strange, "Performance and properties of a solid amine sorbent for carbon dioxide removal in space life support applications," *Energy and Fuels*, vol. 15, no. 2, pp. 250–255, 2001.

[21] H. Huang, R. Yang, D. Chinn, and C. L. Munson, "Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas," *Industrial & Engineering Chemistry Research*, vol. 42, no. 12, pp. 2427–2433, 2003.

[22] X. Xu, C. Song, B. G. Miller, and A. W. Scaroni, "Adsorption separation of carbon dioxide from flue gas of natural gas-fired boiler by a novel nanoporous "molecular basket" adsorbent," *Fuel Processing Technology*, vol. 86, no. 14-15, pp. 1457–1472, 2005.

[23] R. Serna-Guerrero, E. Da'na, and A. Sayari, "New insights into the interactions of CO_2 with amine-functionalized silica," *Industrial and Engineering Chemistry Research*, vol. 47, no. 23, pp. 9406–9412, 2008.

[24] R. Serna-Guerrero, Y. Belmabkhout, and A. Sayari, "Further investigations of CO_2 capture using triamine-grafted pore-expanded mesoporous silica," *Chemical Engineering Journal*, vol. 158, no. 3, pp. 513–519, 2010.

[25] Y. Belmabkhout, R. Serna-Guerrero, and A. Sayari, "Amine-bearing mesoporous silica for CO_2 removal from dry and humid air," *Chemical Engineering Science*, vol. 65, no. 11, pp. 3695–3698, 2010.

[26] P. J. E. Harlick and A. Sayari, "Applications of pore-expanded mesoporous silicas. 3. Triamine silane grafting for enhanced CO_2 adsorption," *Industrial & Engineering Chemistry Research*, vol. 45, no. 9, pp. 3248–3255, 2006.

[27] R. Serna-Guerrero, Y. Belmabkhout, and A. Sayari, "Triamine-grafted pore-expanded mesoporous silica for CO_2 capture: effect of moisture and adsorbent regeneration strategies," *Adsorption*, vol. 16, no. 6, pp. 567–575, 2010.

[28] P. J. E. Harlick and A. Sayari, "Applications of pore-expanded mesoporous silica. 5. Triamine grafted material with exceptional CO_2 dynamic and equilibrium adsorption performance," *Industrial & Engineering Chemistry Research*, vol. 46, no. 2, pp. 446–458, 2007.

[29] N. R. Stuckert and R. T. Yang, "CO_2 capture from the atmosphere and simultaneous concentration using zeolites and amine-grafted SBA-15," *Environmental Science & Technology*, vol. 45, no. 23, pp. 10257–12264, 2011.

[30] C. W. Jones, "CO_2 capture from dilute gases as a component of modern global carbon management," *Annual Review of Chemical and Biomolecular Engineering*, vol. 2, pp. 31–52, 2011.

[31] Y. Belmabkhout, R. Serna-Guerrero, and A. Sayari, "Adsorption of CO_2-containing gas mixtures over amine-bearing pore-expanded MCM-41 silica: application for gas purification," *Industrial and Engineering Chemistry Research*, vol. 49, no. 1, pp. 359–365, 2010.

[32] R. Steeneveldt, B. Berger, and T. A. Torp, "CO_2 capture and storage: closing the knowing-doing gap," *Chemical Engineering Research and Design*, vol. 84, no. 9, pp. 739–763, 2006.

[33] R. O. Idem and A. Bello, "Pathways for the formation of products of the oxidative degradation of CO_2-loaded concentrated aqueous monoethanolamine solutions during CO_2 absorption from flue gases," *Industrial & Engineering Chemistry Research*, vol. 44, no. 4, pp. 945–969, 2005.

[34] Y. Belmabkhout and A. Sayari, "Isothermal versus non-isothermal adsorption-desorption cycling of triamine-grafted pore-expanded MCM-41 mesoporous silica for CO_2 capture from flue gas," *Energy and Fuels*, vol. 24, no. 9, pp. 5273–5280, 2010.

[35] A. Sayari, A. Heydari-Gorji, and Y. Yang, "CO_2-induced degradation of amine-containing adsorbents: reaction products and pathways," *Journal of the American Chemical Society*, vol. 134, no. 33, pp. 13834–13842, 2012.

[36] P. C. Rooney, T. R. Bacon, and M. S. DuPart, *Hydrocarbon Processing*, Ibid Press, Chicago, Ill, USA, 1996.

[37] Annual report on air pollution in 2010, Göteborg, Sweden, R, 2011:10.