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Stabilization of Amine-Containing CO_2 Adsorbents: Dramatic Effect of Water Vapor

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Incorporation of organic amines onto large surface area porous solids via impregnation, postsynthesis grafting, or direct co-condensation as a promising approach for CO_2 capture has gained prominence in recent years.[1–13] When properly designed, such materials exhibit high adsorption capacity, fast CO_2 adsorption and desorption, and low energy requirement for recycling. However, despite the large number of contributions devoted to CO_2 adsorption over amine-containing materials,[14] and despite the utmost importance of the long-term stability of such materials, no studies addressed this issue through extensive recycling. The lifetime of adsorbents, which determines the frequency of their replacement, is a critical property of equal importance as CO_2 adsorption capacity, selectivity, and kinetics with direct impact on the economics of any commercial scale operation. Here we show that, under dry CO_2 adsorption−desorption cycling, amine-containing materials ultimately deactivate even under very mild conditions. We also identify the culprit and provide a method to dramatically enhance the stability of such materials. Furthermore, we demonstrate that deactivated materials may be fully regenerated. The current findings provide a straightforward strategy to using amine-containing CO_2 adsorbents under conditions of unprecedented stability.

Capture of anthropogenic carbon dioxide from large sources of emission such as fossil fuel power plants is a key target in the ongoing effort to mitigate the effect of greenhouse gases on global climate change. Although mature, the liquid phase amine scrubbing technology suffers from inherently high regeneration cost, equipment corrosion, and amine oxidative degradation. As a result, there is a strong tendency to develop recyclable solid sorbents to achieve competitive, less energy intensive acid gas removal alternatives. Most physical CO_2 adsorbents such as 13X zeolite,[15,16] activated carbons,[17,18] unmodified periodic mesoporous silicas,[19] and metal−organic frameworks (MOFs)[20–23] require large pressure and/or temperature gradient between the adsorption and desorption stages to enable both efficient adsorption performances and near complete desorption of CO_2. Moreover, they exhibit relatively low selectivity toward CO_2 and generally low tolerance to water vapor in the gas feed, and their CO_2 separation performance decreases drastically at increasing temperature.

In addition to the above-mentioned attributes, amine-containing adsorbents are often tolerant to the occurrence of moisture in the feed.[24] Because of the very nature of the amine−CO_2 interactions, the CO_2 uptake is actually enhanced by the presence of moisture.[1] Under dry adsorption conditions, surface amine groups interact with CO_2 to form carbamate[25] with a stoichiometric CO_2/N ratio of 0.5, whereas under proper humidity conditions, bicarbonate with a stoichiometric ratio $CO_2/N = 1$ may be formed.[26] In contrast, in the presence of other adsorbents such as zeolites and activated carbons, CO_2 adsorption is severely inhibited by moisture because of unfavorable competition.[27]

Table 1. Properties of Amine-Containing Materials

Amine-containing material	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)	Amine loading	Amine function[a]
MONO	420	0.65	7.2	4.3 mmol/g	I
TRI	367	0.87	9.4	7.9 mmol/g	I, II
PEI	4.5	−	−	50 wt %	I, II, III
UREA	546	0.8	6.1	1.27 mmol/g[b]	

[a] I, primary; II, secondary; III, tertiary amine. [b] Urea groups.

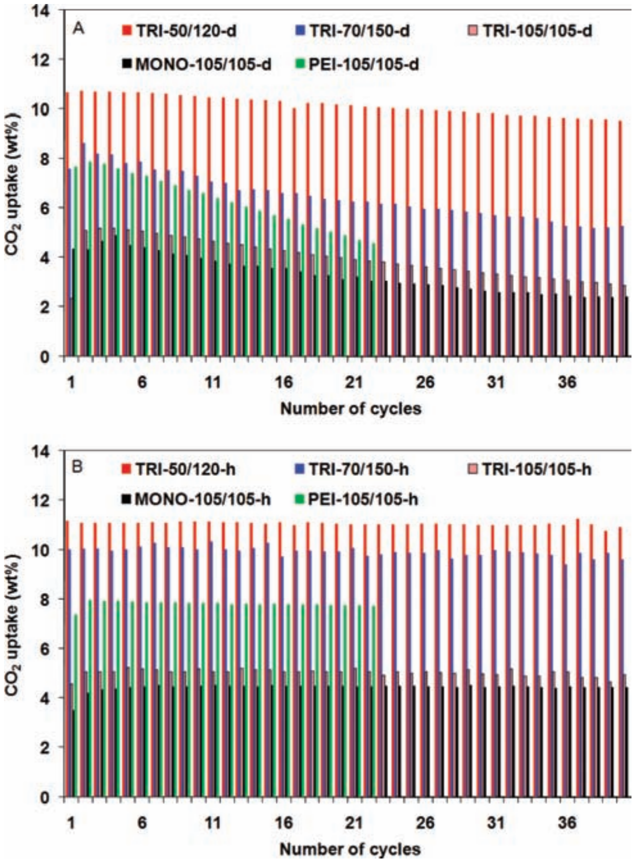

Figure 1. CO_2 adsorption−desorption cycles over different adsorbents, (A) under dry conditions, (B) in the presence of moisture (20 °C as dew point).

This work is concerned with two classes of amine-containing adsorbents for CO_2 removal, namely (i) materials with surface-anchored amine species prepared by aminosilane grafting[1] or co-condensation, or by in situ surface polymerization of reactive amines such as aziridine,[5] and (ii) amine-containing species such as polyethyleneimine, impregnated onto materials with a high surface area and pore volume such as mesoporous silica[7–9] or carbon.[10] Three samples were used to carry out this investigation. These were monoamine and triamine-grafted pore-expanded MCM-41 mesoporous silica (PE-MCM-41) and polyethyleneimine-impregnated

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PE-MCM-41. The preparation of all samples is provided in the Supporting Information. The samples will be referred to as MONO, TRI, and PEI, respectively. Table 1 provides the structural properties and amine content of the materials. The corresponding nitrogen adsorption−desorption isotherms are shown in Figure S1. The PEI-PE-MCM-41 sample was full of polyethyleimine and did not exhibit any porosity.

All the CO_2 adsorption−desorption cycling experiments were carried out at atmospheric pressure. The gas feed (pure CO_2) and the purge gas (pure N_2) used for desorption were either dry or contained a level of moisture corresponding to the equilibrium vapor pressure of water at 20 °C. The actual relative humidity (RH) depends on the temperature of the gas stream, varying from 74% at 25 °C to 0.4% at 150 °C, the highest temperature used for desorption. Under such conditions, the triamine-grafted material undergoing adsorption at *X* °C and desorption at *Y* °C under dry conditions will be referred to as TRI-*X*/*Y*-d. When the cycling experiment is carried out using moisture-containing gases, the material will be designated as TRI-*X*/*Y*-h. Similar nomenclature applies to the other adsorbents, replacing TRI by MONO or PEI.

Figure 1A shows the dynamic CO_2 uptake over a number of adsorption−desorption cycles carried out at different conditions, in the presence of the adsorbents mentioned above. As seen, in all cases, the materials deactivated at a rate that is dependent on the severity of the cycling conditions and on the nature of the adsorbent. The percentage loss of adsorption capacity was 14% for TRI-50/120-d over 40 cycles and as high as 41% for PEI-105/105-d for only 22 cycles. Under the same cycling conditions, adsorbents with grafted amines, MONO-105/105-d and TRI-105/105-d, deactivated by 45% over 40 cycles.

Figure 1B shows the CO_2 adsorption capacity in the same series of experiments as in Figure 1A, except that the feed and the purge gases used for adsorption and desorption were bubbled through a water saturator maintained at 20 °C. As seen, dramatic improvement in the stability of the materials took place. In all cases, the adsorption capacity was stable throughout all cycles.

^{13}C CP MAS NMR data for a series of MONO samples are shown in Figure 2. In addition to signals below 50 ppm, associated with the propyl carbon chain, the fresh sample exhibited a signal at 164.6 ppm attributable to carbamate formed via adsorption of atmospheric CO_2.[28] The MONO-105/105-d, which lost ca. 45% of its adsorption capacity upon CO_2 adsorption−desorption cycling under dry conditions (Figure 1A), exhibited an additional peak at 160.5 ppm. Interestingly, this peak did not occur in MONO-105/105-h, which underwent the same CO_2 cycling, but in humid conditions, i.e., without loss of adsorption capacity. It is thus inferred that such species is responsible for the gradual loss of CO_2 adsorption capacity. To unambiguously identify this species, its ^{13}C CP MAS NMR peak was compared to the signal of the carbon of the urea group in bis(trimethoxysilylpropyl)urea-grafted PE-MCM-41, referred to as UREA. The nitrogen adsorption−desorption isotherm of UREA is reported in Figure S1, whereas its loading and structural characteristics are shown in Table 1. Figure 2 provides direct evidence that the gradual deactivation of the adsorbents is due to the formation of urea groups.

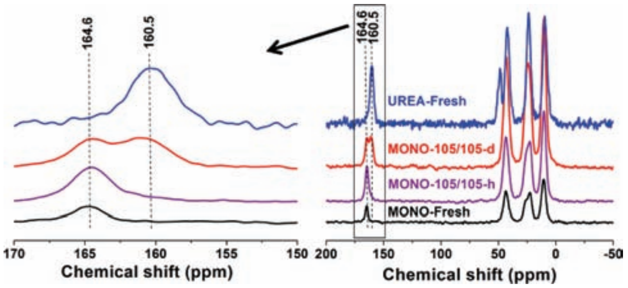


Figure 2. ^{13}C CP MAS NMR spectra for MONO after cycling in dry (MONO-105/105-d) and humid (MONO-105/105-h) conditions as well for fresh MONO (MONO-Fresh) and UREA (UREA-Fresh).

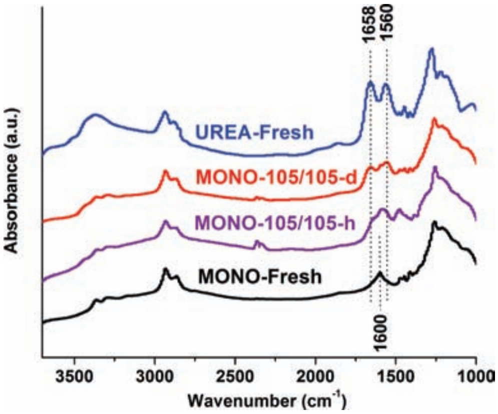


Figure 3. DRIFT spectra for MONO after cycling in dry (MONO-105/105-d) and humid (MONO-105/105-h) conditions as well for fresh MONO (MONO-Fresh) and UREA (UREA-Fresh).

The contention that the formation of stable urea groups, favored under dry conditions, is responsible for the deactivation of the amine-containing CO_2 adsorbents was further substantiated by in situ diffuse reflectance infrared Fourier transform (DRIFT) on MONO. As seen in Figure 3, the spectral region associated with NH_2 scissoring for a fresh MONO sample (MONO-Fresh) was dominated by a band at 1600 cm^{-1}. Cycling CO_2 over this material at 105 °C under dry adsorption and desorption conditions led to the disappearance of the 1600 cm^{-1} band and the development of two bands at 1658 and 1560 cm^{-1}. The corresponding MONO-105/105-h samples cycled in the presence of moisture-containing gases exhibited mainly the 1600 cm^{-1} band, although with a small shoulder at 1650 cm^{-1}. Comparison of these spectra with the DRIFT spectrum of the UREA sample shows clearly that the two new bands in MONO-105/105-d are associated with the occurrence of urea groups.

Figure 4 provides evidence that, under mild, but dry conditions, TRI-70/70-d which seems to be stable over dozens cycles actually deactivates gradually over hundreds of cycles to reach 15% loss after *ca*. 750 cycles. As in the experiments described earlier, humidification of the gas streams led to a stable material over 700 cycles (TRI-70/70-h). In contrast to TRI-70/70-h, examination of the DRIFT spectrum of TRI-70/70-d (not shown) indicated the presence of urea groups. Thus, the development of urea groups occurs even under mild conditions, albeit at a much slower rate.

Scheme 1A shows the relationship between amine, CO_2, carbamate, and urea species during CO_2 adsorption−desorption under dry conditions. The urea groups may form readily by direct interaction between amine species and CO_2 at high temperature. Drage et al.[29] carried out temperature programmed adsorption of CO_2 on polyethyleneimine-loaded silica. As the temperature increased, a weight loss corresponding to the decomposition of carbamate species took place. Starting at *ca*. 135 °C, they observed a weight increase corresponding to a secondary reaction between CO_2 and amine groups, leading to the formation of urea groups. The current work shows that under repeated CO_2 adsorption, provided that the gas streams are dry, urea will form incrementally during adsorption and/or desorption directly or via carbamate decomposition, even under mild conditions. Accumulation of heat-

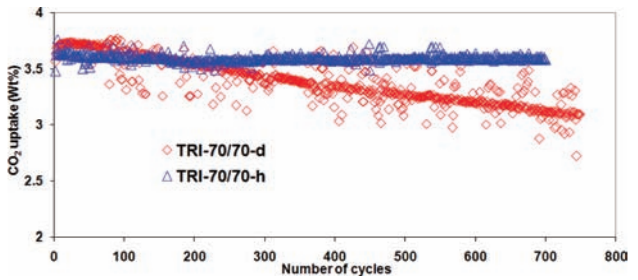


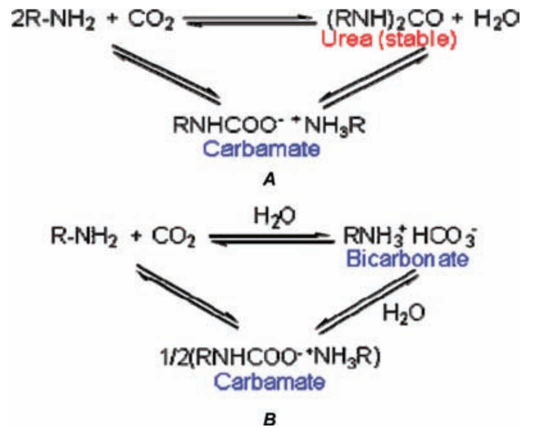
Figure 4. CO_2 adsorption−desorption cycles on TRI-PE-MCM-41 in dry (TRI-70/70-d) and humid (20 °C as dew point, 7.5% RH) (TRI-70/70-h) conditions.

resistant urea groups leads ultimately to gradual loss of CO_2 uptake. In contrast, Scheme 1B shows that if moisture-containing gases are used, the formation of urea is strongly inhibited. Indeed, even at a relative humidity as low as 0.4% as in the case of TRI-70/150-h, the material did not deactivate despite the high desorption temperature (Figure 1B). Moreover, based on Figure 1, and DRIFT data (not shown), it is inferred that the formation of urea groups and their inhibiting effect on CO_2 adsorption also occur for polyethyleneimine-impregnated PE-MCM-41, and most likely other types of amine-supported materials.

Deactivation via formation and accumulation of urea groups can be completely reversed via hydrolysis of such groups, while preserving the integrity of the material. Heating severely deactivated MONO-105/105-d at 200 °C under a flow of nitrogen containing as little as 0.15% RH (dew point at 20 °C) for 24 h restored the grafted propylamine completely, as demonstrated by ^{13}C CP MAS NMR, DRIFT data and CO_2 adsorption measurements (not shown). Moreover, as evidenced by ^{13}C CP MAS NMR, and DRIFT (not shown), the UREA sample was also successfully hydrolyzed under similar conditions to generate a propylamine-grafted material with an equilibrium CO_2 adsorption capacity of *ca.* 1.21 mmol/g (CO_2/N = 0.48) at room temperature and 1 atm using 5% CO_2/N_2.

This work provides key data regarding the deactivation and regeneration of amine-modified CO_2 adsorbents and a simple strategy to recycle such materials hundreds, or more likely thousands, of times without loss of performance. It paves the way to using amine-containing materials for CO_2 separation and gas purification under conditions of high stability. The enhanced stability, combined with the desirable attributes listed earlier, will make adsorption over amine-containing materials a competitive route to CO_2 separation from industrial gases such as flue gas, syngas, and biogas as well as the purification of gases such as hydrogen and air. Among the different possibilities, steam or moisture-containing nonadsorbing gases or CO_2 may be used as a purge gas, providing opportunities to separate pure CO_2. The use of moisture-containing purge gas may be combined with appropriate temperature or pressure swing operation.

Scheme 1



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Supporting Information Available: Material preparation, material characterization, CO_2 adsorption−desorption measurements, N_2 adsorption−desorption isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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