JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

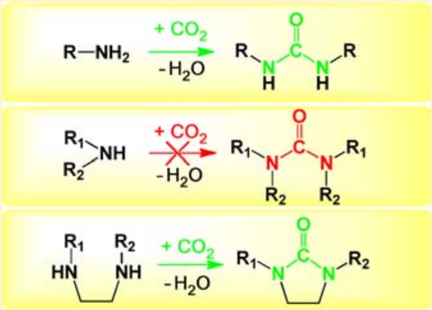
# $CO_2$-Induced Degradation of Amine-Containing Adsorbents: Reaction Products and Pathways

Abdelhamid Sayari,* Aliakbar Heydari-Gorji, and Yong Yang

Department of Chemistry, Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, Ontario, K1N 6N5 Canada

*Supporting Information*

**ABSTRACT:** A comprehensive study was conducted to investigate the stability of a wide variety of mesoporous silica-supported amine-containing adsorbents in the presence of carbon dioxide under dry conditions. $CO_2$-induced degradation of grafted primary and secondary monoamines (pMono, sMono), diamines with one primary and one secondary amines (Diamine) and triamine with one primary and two secondary amines (TRI) as well as different impregnated polyamines such as branched and linear polyethylenimine (BPEI and LPEI) and polyallylamine (PALL) was investigated using extensive $CO_2$ adsorption−desorption cycling as well as diffuse reflectance infrared Fourier transform (DRIFT) and $^{13}C$ CP MAS NMR measurements. Except for sMono, all other supported amines underwent significant deactivation in the presence of dry $CO_2$ under mild conditions. In all cases, the decrease in $CO_2$ uptake was associated with the formation of urea linkages at the expense of amine groups. The urea-containing species were identified, and the deactivation pathways were delineated.



## 1. INTRODUCTION

The selective removal of $CO_2$ from gaseous streams is a subject of widespread industry and public concern. Currently, a variety of technologies, such as physical and chemical absorption with solvents, membrane separation and adsorption on solid materials, have been proposed.[1] With regard to the latter, extensive research activities focused on the development of grafted[2−6] and impregnated[7−18] amine-containing species on large surface area supports. Several authoritative reviews on this topic are readily available.[19−22] Most literature reports were devoted to the measurements of equilibrium or near-equilibrium adsorption capacity of materials using $CO_2$-containing gas mixtures. However, only a limited number of contributions dealt with the stability of amine-modified adsorbents in the presence of $H_2S$,[7,23] $NO_2$,[6] $SO_2$,[24] $O_2$,[25−27] moisture,[28,29] and $CO_2$[28−31] on the carbon dioxide adsorptive properties, most often without delineating the mechanisms of deactivation. Of utmost importance in this context is the stability of the adsorbents under conditions favorable for the recovery of a pure $CO_2$ stream, ready for compression and sequestration,[1] or for other usages such as oil enhanced recovery and as raw material for high value added chemicals.[32] To achieve this goal, two scenarios have been contemplated. The first approach, which consists of using low quality steam as a purge gas is facing challenging issues associated with the lack of stability of the materials pore structure in the presence of steam.[33,34] The second alternative would be to use $CO_2$ as a purge gas in a temperature swing operation. To achieve this objective, it would be necessary to investigate the stability of different amine-containing adsorbents in the presence of $CO_2$ at relatively high temperature to mimic the desorption conditions in the presence of $CO_2$ purge gas.

Drage et al.[30] investigated the behavior of branched polyethylenimine (PEI)-impregnated silica in pure $CO_2$ at different temperatures. Beyond 135 °C, they observed a weight gain paralleled by a decrease in adsorption capacity. This was attributed to the formation of urea linkages. Sayari and Belmabkhout[28] investigated the effect of $CO_2$ on several amine-containing adsorbents under different temperature swing conditions. They found that (i) all materials deactivated at different rates depending on the severity of the adsorption and desorption conditions, (ii) the deactivation was due to the formation of stable urea groups at the expense of amine, and (iii) none of the materials deactivated when humidified gases were used instead of dry gases. In a more detailed study, Sayari et al.[31] investigated the effect of dry $CO_2$ on the adsorptive properties of grafted propylamine (pMono containing a single primary amine), *N*-methylpropylamine (sMono with a single secondary amine) and propyldiethylenetriamine (TRI with one primary and two secondary amine groups). They found that while pMono deactivated readily, sMono was stable even at temperatures as high as 200 °C. This finding was associated with the occurrence of isocyanate as intermediate species toward the formation of urea groups. Since the secondary monoamine cannot generate isocyanate, it did not undergo $CO_2$-induced coupling into urea. However, the deactivation of TRI was higher than expected based on complete transformation of the primary amine groups into urea linkages. This indicated that once the isocyanate is formed, it can react with either a primary or a secondary amine to yield different ureas. Heydari-Gorji et al.[29] carried out a multifaceted investigation

**Received:** June 8, 2012
**Published:** July 30, 2012

on thermal, oxidative and $CO_2$-induced degradation of branched PEI-impregnated mesoporous silica. They demonstrated that in the presence of dry $CO_2$, the adsorbent degraded through the formation of open chain and/or cyclic ureas, even under mild conditions. However, consistent with earlier studies,[28] it was also shown that the formation of urea groups may be completely inhibited in the presence of moisture.

In light of the foregoing discussion, one important question arises: What would be the behavior of an all-secondary amine polymer such as linear polyamine, in the presence of dry $CO_2$? To address this question and to gain further insights into the $CO_2$-induced deactivation processes, we embarked on a comprehensive study dealing with a wide variety of amine-containing adsorbents. Using $CO_2$ uptake measurements as well diffuse reflectance infrared Fourier transform spectroscopy and solid-state NMR data, different deactivation processes were delineated. Depending on the structure of the adsorbing materials and the nature of the amine groups involved, several degradation mechanisms were proposed.

## 2. EXPERIMENTAL SECTION

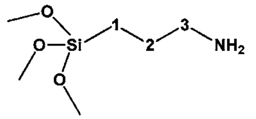
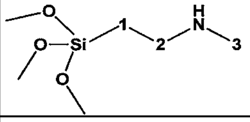
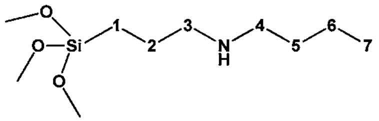
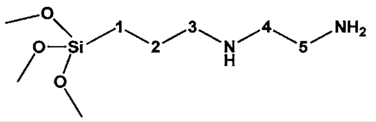
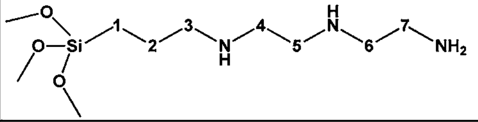
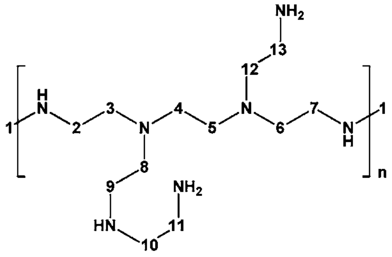
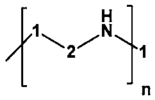
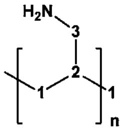
**2.1. Materials and Synthesis of Adsorbents.** Linear PEI was supplied by Polysciences, Inc. All other chemicals were obtained from Sigma-Aldrich and Gelest. All amines and polyamines used in this work are listed in Table 1. Carbon dioxide (99.99%) and nitrogen (99.999%) were supplied by Linde Canada.

The detailed preparation procedure for amine-grafted pore-expanded MCM-41 (PE-MCM-41) may be found elsewhere.[2] Briefly, samples referred to as pMono, sMono-1, sMono-2, Diamine, and TRI were prepared by surface grafting of 3-(aminopropyl)trimethoxysilane, trimethoxy[3-(methylamino)propyl]silane, *N*-butylaminopropyl trimethoxysilane, *N*-[3-(trimethoxysilyl)propyl]ethylenediamine, and $N^1$-(3-trimethoxy-silylpropyl)diethylenetriamine. After drying PE-MCM-41 silica in a vacuum oven at 120 °C, the support material was loaded into a multineck glass flask containing 100 mL of toluene. Once a homogeneous mixture was produced, 0.1−0.4 mL of distilled deionized water/g of PE-MCM-41 was added and left stirring for 30 min. The flask equipped with a condenser was then submerged in a silicon oil bath set at 85 °C using a temperature-controlled stirring hot plate with an external temperature probe. Monoaminosilanes (2 mL per gram of silica) or di- and triaminosilane (3 mL/g of silica) was subsequently added to the mixture and left stirring overnight. The products were filtered and washed with toluene and pentane. The recovered solid materials were dried at room temperature overnight.

Polyamine-impregnated materials were prepared using as support a large pore SBA-15 silica (12.5 nm) synthesized according to literature reports.[35,36] Typically, 2.4 g of Pluronic P123 triblock copolymer was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 40 °C. Then, 8.5 g of tetraethylorthosilicate was added into the solution with stirring at 40 °C for 20 h. The mixture was then transferred into an autoclave for further treatment at 130 °C overnight without stirring. The material was air-calcined at 550 °C to remove the template.

Regarding the preparation of impregnated adsorbents, the required amount of branched PEI (Aldrich, average $M_n$ ~ 600), linear PEI (Polysciences, Inc., $M_w$ ~ 2500) or polyallylamine (Aldrich, $M_w$ ~ 17000, 20% in water) was dissolved in methanol before adding the mesoporous silica support. The resultant slurry was stirred at room temperature until the solvent is evaporated, then the sample was further dried at 50 °C under reduced pressure (600 mmHg). The adsorbents were denoted as BPEI, LPEI, or PALL for branched PEI, linear PEI, or polyallylamine supported on SBA-15 mesoporous silica, respectively. The structural properties of the adsorbents are listed in Table S1 (Supporting Information). Notice however, that the current adsorbents were not optimized for maximum $CO_2$ uptake, because this was not the main purpose of this work.

**Table 1. List of Amines Used**

| amine | structure |
|---|---|
| pMono |  |
| sMono-1 |  |
| sMono-2 |  |
| Diamine |  |
| TRI |  |
| BPEI |  |
| LPEI |  |
| PALL |  |

**2.2. Adsorption Measurements.** $CO_2$ adsorption and temperature swing adsorption (TSA) measurements were carried out using a Rubotherm magnetic suspension balance. Details about the experimental setup and procedure may be found elsewhere.[5] To investigate the deactivation of the adsorbents in the presence of dry $CO_2$, after nitrogen pretreatment at the desorption temperature (130−160 °C) for 90 min, the sample was cooled down to the adsorption temperature (50 or 100 °C) before switching to a pure $CO_2$ stream. After 30 min of exposure, the regeneration took place at the desorption temperature under flowing pure $CO_2$ at atmospheric pressure for 30 min; then cooled again to the adsorption temperature. The cooling stage followed by adsorption was carried out in pure $CO_2$ atmosphere, and took a total of 100 min. The procedure was repeated over several cycles. At the end of the cycling experiment, the adsorbent was regenerated using pure $N_2$ at the same desorption temperature and the $CO_2$ uptake was measured at the adsorption temperature in order to compare with the fresh material. The same procedure was carried out for all adsorbents. The $CO_2$ uptake was calculated based on the weight gain of the sample during adsorption. The degree of deactivation represents the difference between the uptakes of the fresh and $CO_2$-exposed materials relative to the original uptake. The adsorbents after TSA cycling were designated as Adsorbent-$T_{ads}/T_{des}$, where $T_{ads}$ and $T_{des}$ are the adsorption and desorption temperatures, respectively. For example, pMono-50/130 means grafted primary monoamine adsorbent after TSA cycling at 50 °C for adsorption and 130 °C for desorption.

**2.3. Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy and Nuclear Magnetic Resonance (NMR).** A Nicolet Magna-IR 550 spectrometer equipped with a MCT detector and a Thermo diffuse reflectance cell was used to collect DRIFT spectra. About 15 mg of powder sample was placed in the cell and pretreated in flowing ultrahigh purity He at 100 °C for 2 h. The DRIFT spectra were then recorded under He atmosphere for fresh and $CO_2$-deactivated materials. The spectrum for KBr was used as background. The $^{13}C$ CP/MAS NMR experiments were conducted on a Bruker AVANCE 200 or 400 instrument. The spinning frequency was set to 4.5 and 10 kHz for Avance 200 and 400, respectively. The contact time was 2 ms, with recycle delays of 2 s. Before NMR measurements, all samples were pretreated using pure $N_2$ at the same temperature as the desorption temperature to release adsorbed $CO_2$, if any.

## 3. RESULTS AND DISCUSSION

Figure 1a,b presents the working capacity data during TSA cycling in the presence of dry pure $CO_2$ for different adsorbents. Pure $CO_2$ was used for both adsorption and desorption steps for 30 cycles.

Table 2 shows the corresponding uptake losses for all adsorbents after 30 TSA cycles. As seen, all grafted materials, with the exception of sMono-1 and sMono-2, lost more than 65% of their original $CO_2$ adsorption capacity. With regard to the three impregnated polyamines, although they all underwent significant decrease in $CO_2$ uptake, the degree of deactivation seems to decrease with increasing molecular weight, most likely because of increasing diffusion resistance. After 30 TSA cycles at 50/130 °C, BPEI ($M_n \sim 600$) showed 72% $CO_2$ capacity loss versus 50% for LPEI ($M_w \sim 2500$), whereas PALL ($M_w \sim 17\,000$) had to be treated under more severe condition (30 cycles at 100/160 °C) to reach a high degree of deactivation (62%), suitable for DRIFT and NMR measurements. Under otherwise the same conditions, increasing the desorption temperature in the presence of LPEI, to 150 °C, led to 78% deactivation versus 50% for desorption at 130 °C. Similarly, PALL-100/160 showed 82% uptake loss upon continuous exposure to dry pure $CO_2$ at 180 °C for 10 h.

**Table 2. $CO_2$ Uptake Loss of the Adsorbents after Adsorption−Desorption Cycling at 50/130 °C**

| adsorbent | uptake loss (wt%) | organic content (wt%) |
|---|---|---|
| pMono | 66 | 28 |
| sMono-1 | <1 | 26 |
| sMono-2 | <1 | 29 |
| Diamine | 72 | 24 |
| TRI | 72 | 37 |
| BPEI | 76 | 50 |
| LPEI | 50[a] | 40 |
| PALL | 62[b] | 40 |

[a] Uptake loss after 30 adsorption−desorption cycles at 50/150 °C was 78%. [b] Adsorption−desorption cycles at 100/160 °C.

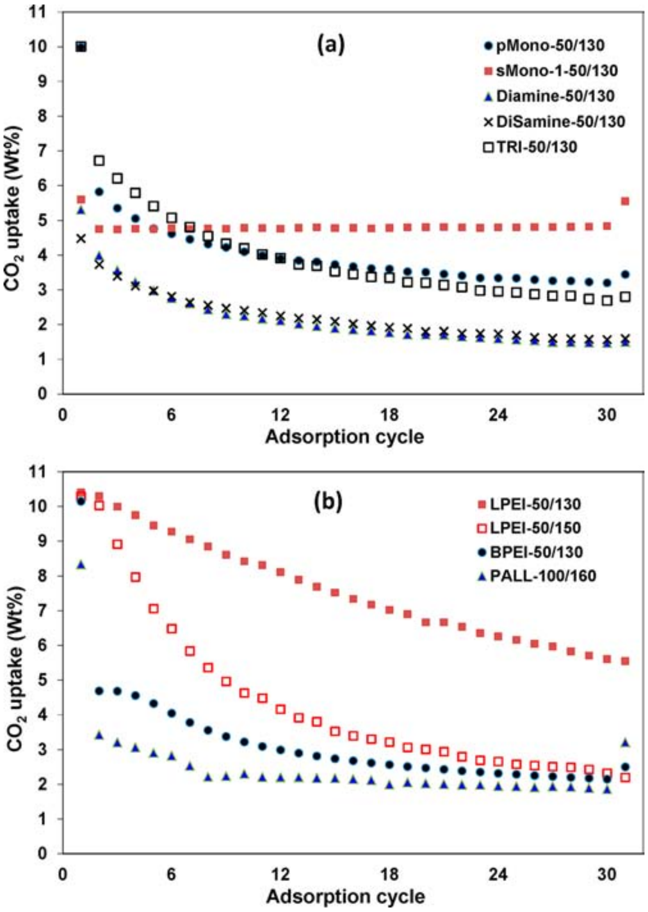
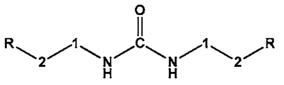
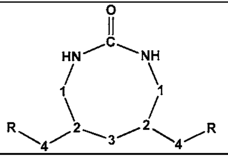
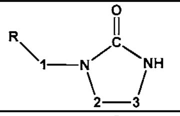
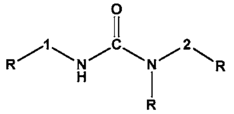
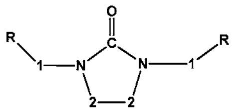
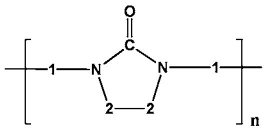


**Figure 1.** $CO_2$ uptake during TSA cycling over (a) amine-grafted, (b) amine-impregnated adsorbents in dry condition (cooling and adsorption at 50 or 100 °C and 1 bar using pure $CO_2$ for 100 min and desorption at 130−160 °C and 1 bar using pure $CO_2$ for 30 min).

On the basis of earlier findings[28−31] and the following discussion of FTIR and $^{13}C$ NMR data, it is inferred that the $CO_2$-induced deactivation of supported amines under dry condition takes place through the formation of stable urea linkages at the expense of amine groups. Table 2 shows that the sMono samples did not suffer any deactivation, indicating that single secondary monoamines cannot form open-chain urea linkages under our experimental conditions.

Table 3 presents a comprehensive list of urea derivatives that may form upon dry $CO_2$-induced degradation of the supported amines listed in Table 1. Two primary amines in separate chains react with $CO_2$ to form a disubstituted urea type U-1. Two primary amines in a single chain, such as PALL, react with carbon dioxide to produce a cyclic urea with an eight-membered ring, that is, U-2. As far as FTIR and NMR measurements are concerned, since the ring is too large, species U-2 behaves like U-1. Notice that none of the amine-containing materials used here is capable of generating primary amine-derived ureas with smaller cycles. Interestingly, a primary amine can react with $CO_2$ and a secondary amine in the same chain or in a different molecule to form an *N*-substituted cyclic urea (U-4) or trisubstituted open-chain urea (U-3).[29] Moreover, *N,N′*-disubstituted cyclic ureas, U-5 and U-6, are formed via reaction of two secondary amines in a single chain with $CO_2$. Table 3 also shows the range of $^{13}C$ NMR shift for **C**=O in the different urea groups as determined by the ACD/C+H NMR Predictors software. These data are consistent with experimental measurements reported in the literature.[37,38] They may be divided into two groups of ureas with **C**=O chemical shifts in the range of (i) 159−161 ppm associated with disubstituted (U-1, U2 with large cycle) and trisubstituted (U-4) open-chain ureas as well as *N,N′*-disubstituted cyclic ureas (U-5), and (ii) 163.5−165 ppm attributed to *N*-substituted cyclic ureas (U-3).

**Table 3. List of Possible Urea Derivatives Formed by $CO_2$-Induced Deactivation of Supported Amines**

| urea | structure | $^{13}$C chemical shift of *C*=O |
|---|---|---|
| U-1 |  | 159.5-160.5 |
| U-2 |  | 159.5-160.5 |
| U-3 |  | 163.5-165 |
| U-4 |  | 159.5-160.5 |
| U-5 |  | 160-161 |
| U-6 |  | 162-163 |

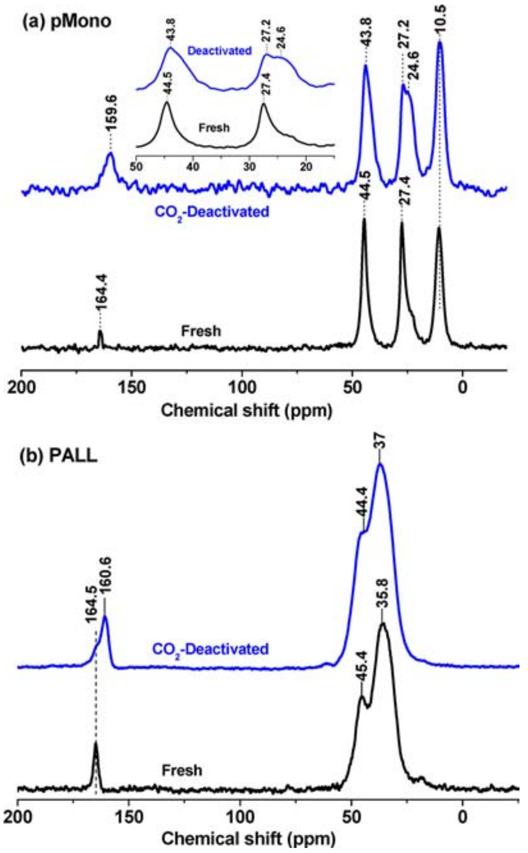


**Figure 2.** $^{13}$C CP MAS NMR spectra of (a) pMono before and after TSA cycling in dry $CO_2$ at 50/130 °C and (b) PALL before and after TSA cycling in dry $CO_2$ at 100/160 °C.

Nonetheless, polymer containing adjacent imidazolidinone entities (U-6) exhibits a **C**═O chemical shift at 162−163 ppm.

$^{13}$C NMR and DRIFT data for $CO_2$-deactivated supported amines provide strong evidence to the formation of different urea linkages. Figures 2−4 show the $^{13}$C CP/MAS NMR spectra for fresh and $CO_2$-deactivated materials. In the following discussion, the methylene groups in fresh adsorbents and in the corresponding ureas will be designated as C*x* and CU*x*, respectively, where *x* is the carbon number as shown in Tables 1 and 3.

$^{13}$C NMR data for pMono and PALL are shown in Figure 2. As seen in Figure 2a, fresh pMono exhibited three signals at 10.5, 27.3, and 44.5 ppm corresponding to C1, C2, and C3 in the propyl chain. A small signal at ca. 164.4 ppm corresponds to carbamate, due to $CO_2$ adsorption from ambient air. This peak appeared in the $^{13}$C NMR spectrum of all fresh adsorbents. Upon $CO_2$-induced deactivation, NMR signals corresponding to C1 and C2 hardly changed, while three new peaks appeared for pMono-50/130 at 24.6, 43.8, and 159.6 ppm (Figure 2a). Consistent with the formation of urea type U-1 (Table 3), these signals were assigned to CU2, CU1, and **C**═O, respectively. The peaks centered at 35.8 and 45.4 ppm in Figure 2b were assigned to C1−C2 and C3 (Table 1) in fresh PALL, respectively. After extensive $CO_2$ adsorption−desorption cycling, the slightly shifted peaks at 37 and 44.4 ppm were attributed to CU2 to CU4 and CU1 in the formed urea, that is, U-2 (Table 3). Interestingly, the new peak at 160.6 ppm assigned to **C**═O in U-2 proved the formation of disubstituted urea. The small shoulder at 164.5 was possibly a remnant of the carbamate signal.

As seen here and elsewhere,[31] adsorbents containing single secondary amine species, sMono-1 and sMono-2, were exceedingly stable in dry $CO_2$. However, grafted materials containing ethylenediamines with mixed primary and secondary amines such as Diamine and TRI underwent significant deactivation upon exposure to dry $CO_2$ (Table 2). Figure 3a,b presents the $^{13}$C NMR data for both fresh and $CO_2$-deactivated Diamine and TRI adsorbents.

Figure 3a shows the $^{13}$C NMR data for Diamine before and after TSA cycling in dry $CO_2$ at 50/130 °C. The observed peaks centered at 9.5, 22, 40.3, 47.5, 50.8, and 164 ppm for fresh Diamine were associated with C1, C2, C5, C3, C4 (Table 1) and carbamate. Upon $CO_2$-deactivation, the NMR peaks for the carbon atoms adjacent to the amine groups (C3 to C5) disappeared, and two new peaks were observed at 38.6 and 45.5 corresponding to CU3 and CU1-CU2 (Table 3), respectively. The peak at 164 ppm grew, but hardly shifted. Since the material has been 72% deactivated (Table 2), this peak cannot correspond to a carbamate species, but to **C**═O in U-3 (Table 3) urea. This finding shows that the formation of *N*-substituted cyclic urea (U-3) between two amine groups in a single chain is more favorable than open-chain disubstituted urea (U-1) because no peak was observed at ca. 160 ppm. Notice that based on the behavior of sMono, open-chain tetrasubstituted urea cannot be formed between secondary amines in different chains, under our adsorption−desorption conditions of $CO_2$−containing dry gases.

TRI with two secondary amines and one primary amine degraded in the presence of dry $CO_2$ mostly via the formation

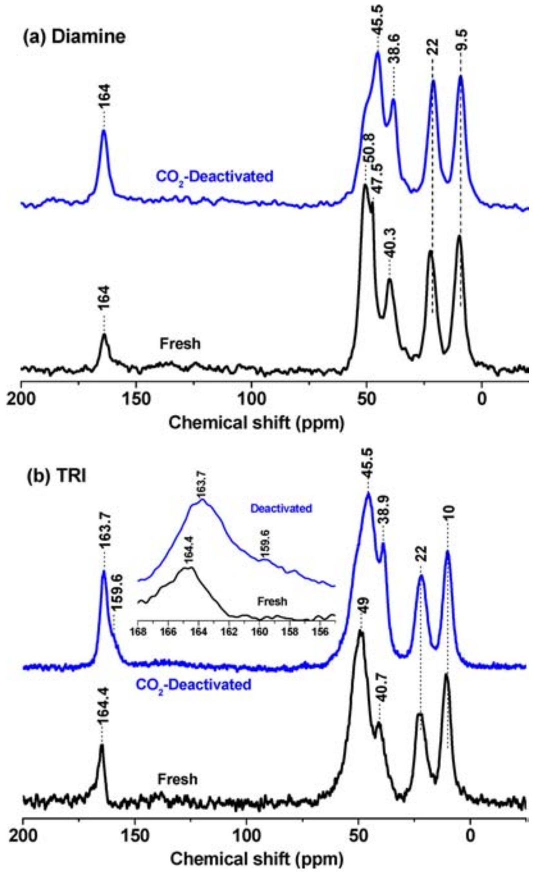


**Figure 3.** $^{13}C$ CP MAS NMR spectra of (a) Diamine, (b) TRI, before and after TSA cycling in dry $CO_2$ at 50/130 °C.

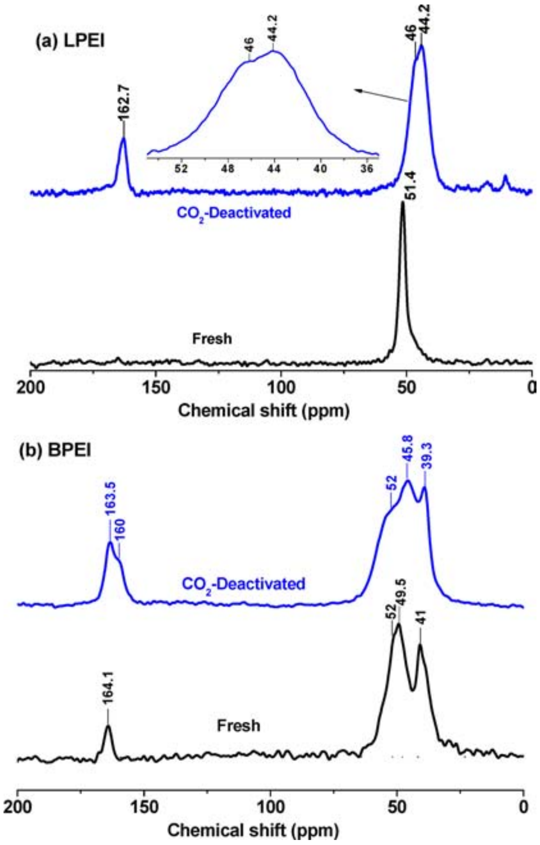


**Figure 4.** $^{13}C$ CP MAS NMR spectra of (a) BPEI, (b) LPEI before and after TSA cycling in dry $CO_2$ at 50/130 and 50/150 °C, respectively.

of cyclic urea (U-3). Figure 3b shows that $CO_2$-deactivated TRI exhibits three peaks at 38.9, 45.5, and 163.7 attributable to CU3, CU1–CU2, and **C**═O in U-3 urea. A small shoulder at 159.6 ppm may indicate the formation of type U-5 urea via cyclization using two neighboring secondary amines. Although less likely, this peak may correspond to an open-chain type U-1 urea, formed between two primary amine groups in different chains.

The $^{13}C$ NMR data for fresh and $CO_2$-deactivated LPEI are shown in Figure 4a. In contrast to BPEI which contains primary, secondary and tertiary amine groups, LPEI is a polymer composed of only secondary amines with identical local environments. The single $^{13}C$ peak at 51.4 ppm is attributable to the only type of carbon atoms in the polymer chain. Upon $CO_2$-deactivation, two new peaks developed at 44.2 and 46 ppm which were assigned to CU2 and CU1 in urea U-5 (Table 3), respectively. Another peak attributable to **C**═O in U-5 appeared at 162.7 ppm, indicating the occurrence of 5-membered ring cyclic urea (poly-1,3-dimethylene-2-imidazolidinone) as the only $CO_2$-degradation product, with no open-chain urea formed because no peak was observed at 164–165 ppm. Consistent with the experimental data, the ACD/C+H NMR Predictors software indicates that the chemical shift associated with **C**═O in a single U-5 species is expected at 160–161 ppm, while in a polymer containing adjacent U-5 species, the signal shifts to 162–163 ppm.

Figure 4b shows the $^{13}C$ NMR spectrum for fresh and $CO_2$-deactivated BPEI. For fresh BPEI, the peaks at 41, 49.5, and 58 ppm are associated with the methylene groups adjacent to primary (39–41 ppm), secondary (49–52 ppm), and tertiary (52–58 ppm) amine groups.[39] Upon $CO_2$ deactivation, the NMR spectrum underwent significant changes, except for the chemical shift attributable to the carbon atoms attached to tertiary amines (52 ppm). It is thus inferred that tertiary amines were not involved in the $CO_2$-induced degradation process. On the basis of the deactivation mechanism and the degradation products of other amine-containing species discussed above, it is proposed that in the presence of dry $CO_2$, BPEI deactivates through the formation of different kinds of open-chain and cyclic ureas (Table 3). The new peaks at 39.3 and 45.8 ppm were assigned to $-\mathbf{C}H_2-NH-CO-$ in open chain ureas such as CU1 in U-1, U-2 or U-4 or to methylene groups adjacent to cyclic ureas such as CU1 in U-3, U-5 or U-6. Two new peaks appeared at 160 and 163.5 ppm that may be assigned to **C**═O in different open chain or cyclic ureas (Table 3), involving primary and secondary amines.

Figures 5, 6 and 7 show the DRIFT spectra for all adsorbents before and after TSA cycling in dry pure carbon dioxide. Table 4 shows the wavenumbers of relevant infrared bands in fresh and deactivated materials and their assignments.[4,40]

As seen in Figure 5a,b, the disappearance of the 1600 $cm^{-1}$ band associated with $NH_2$ deformation and the parallel development of two new bands at 1565 and 1653–1660 $cm^{-1}$ provide strong evidence for the formation of U-1 and U-2 ureas in pMono and PALL, respectively. The DRIFT spectra for $CO_2$-deactivated Diamine, TRI and LPEI are shown in Figure 6, panels a, b, and c, respectively. The new bands observed at ca. 1500 and 1700 $cm^{-1}$ for all these adsorbents were associated with C–N and C═O stretch in cyclic ureas, that is, U-3, U-5 and U-6.

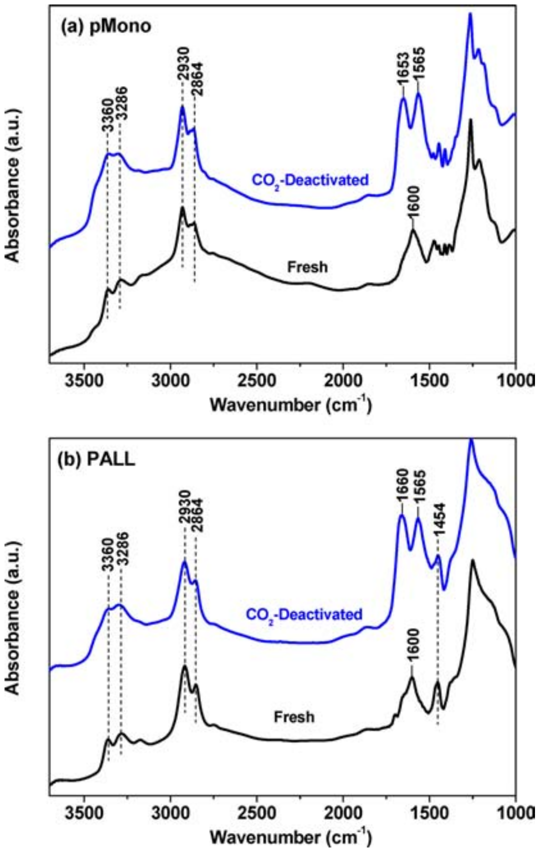


**Figure 5.** DRIFT spectra for (a) pMono and (b) PALL, before and after TSA cycling in dry $CO_2$ at 50/130, 100/160, respectively.

Figure 7 indicates that conversely to other amine-containing adsorbents, BPEI-50/130 shows four new DRIFT absorption bands at 1560 and 1660 and also 1498 and 1702 cm$^{-1}$, associated with linear and cyclic ureas (Tables 3 and 4), respectively. Consistent with $^{13}$C NMR data, this finding provides direct evidence that several kinds of substituted ureas were formed.

**3.1. Deactivation Mechanisms.** Two general mechanisms for the formation of urea from amines in the presence of $CO_2$ will be considered, namely, dehydration of ammonium carbamate, and reaction of amine with isocyanate, the latter stemming from primary amine. Scheme 1 proposes a number of possible pathways for the degradation of primary and secondary amine groups in the presence of $CO_2$ under dry conditions.

On the basis of the current experimental results and literature data,[31] it is inferred that the formation of open-chain urea most likely involves at least one primary amine, indicating that no open-chain tetrasubstituted urea, involving two secondary amine groups, may be formed. Mechanism A, Route 1 (Scheme 1) seems to be the most dominant pathway. A primary amine reacts with $CO_2$ to form the corresponding carbamic acid, which in turn, dehydrates under dry conditions, particularly at high temperature to form the corresponding isocyanate. The latter condenses with a primary or secondary amine to yield di- and trisubstituted open-chain ureas, respectively.

Wu et al.[41] reported an effective process for the synthesis of urea derivatives from monoamines and $CO_2$ without any catalyst or organic solvent, and showed that under high temperature and $CO_2$ pressure (180 °C, 10 MPa), primary monoamines afford disubstituted ureas in moderate to high yields. Using mixtures of primary and secondary monoamines, they obtained significant yields of both primary amine-derived disubstituted ureas and mixed amine-derived trisubstituted ureas, but no tetrasubstituted ureas from secondary amines only. Likewise, Ion et al.[42] found that even in the presence of basic catalysts such as $Cs_2CO_3$, secondary monoamines alone do not form urea in the presence of $CO_2$ (2.5 MPa, 170 °C, 24 h), whereas mixed primary and secondary monoamines afford di- and trisubstituted ureas, without any tetrasubstituted urea. These findings may be explained by the occurrence of primary amine-derived isocyanate as an intermediate, followed by reaction with either primary or secondary amine into ureas. Our results regarding the deactivation of monoamines, or the lack thereof are fully consistent with such observations. Notice, however, that secondary monoamines may generate tetrasubstituted ureas in the presence of strong bases such as KOH on

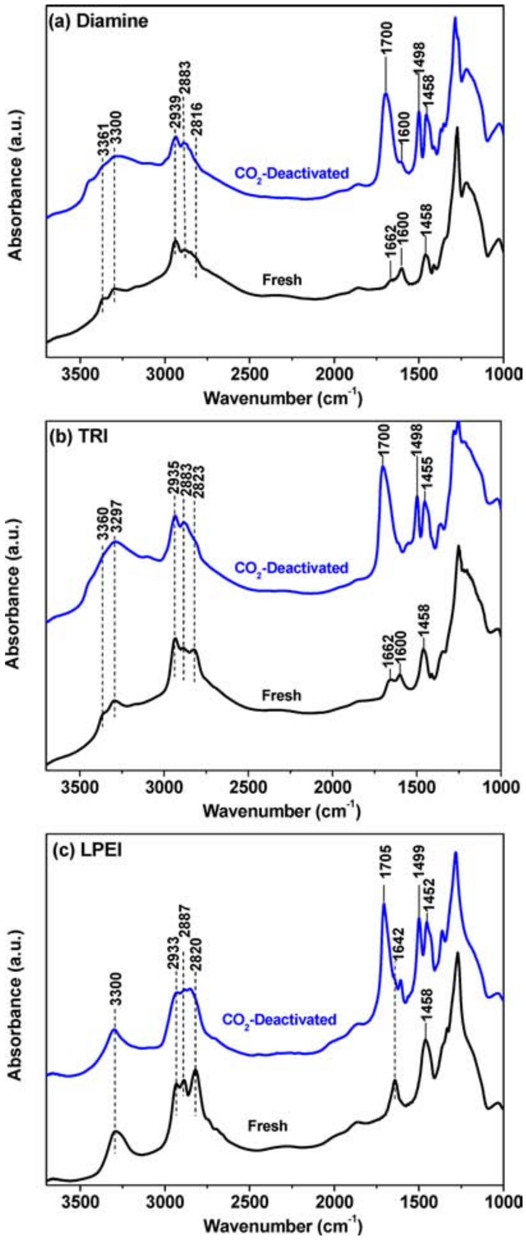


**Figure 6.** DRIFT spectra for (a) Diamine, (b) TRI and (c) LPEI before and after TSA cycling in dry $CO_2$ at 50/130 °C (a and b) or 50/150 °C (c).

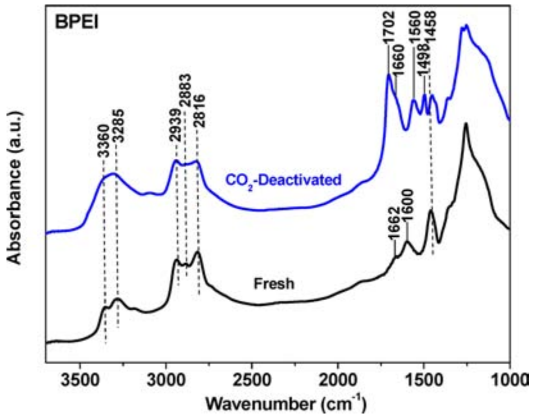


**Figure 7.** DRIFT spectra for BPEI before and after TSA cycling in dry $CO_2$ at 50/130 °C.

**Table 4. Assignments of DRIFT Absorption Bands**

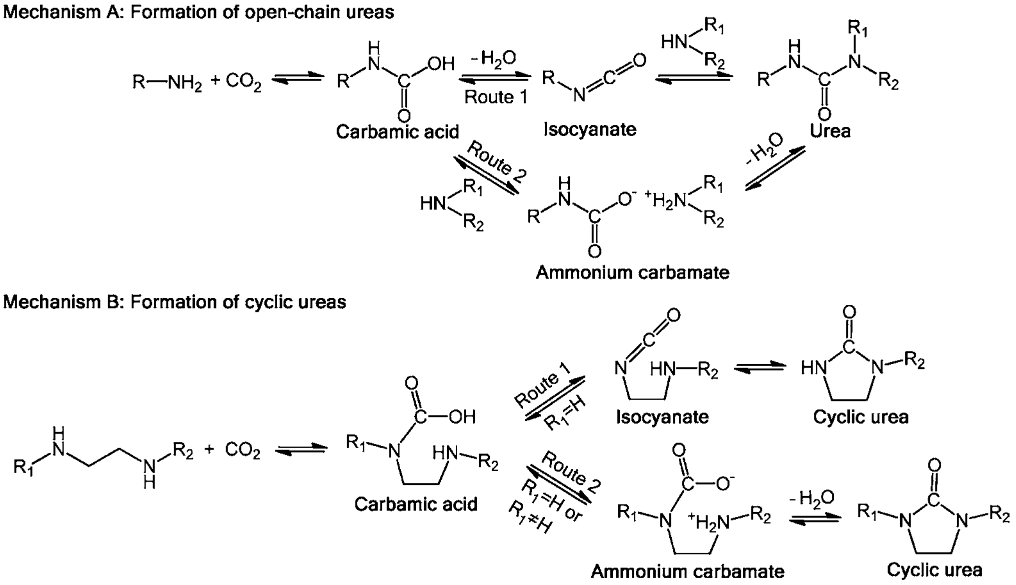
| frequency (cm$^{-1}$) | assignment |
|---|---|
| 1450–1460 | $CH_2$ deformation |
| 2815–2940 | $CH_2$ stretch |
| 1595–1600 | $NH_2$ deformation |
| 1630–1660 | $NH_3^+$ deformation |
| 3286–3300 | NH stretch and symmetric $NH_2$ stretch |
| 3360 | asymmetric $NH_2$ stretch |
| 1498–1500 | C–N stretch in U-3/U-5/U-6 |
| 1560–1565 | C–N stretch in U-1/U-2 |
| 1653–1660 | C═O stretch in U-1/U-2 |
| 1700–1705 | C═O stretch in U-3/U-5/U-6 |

polyethylene glycol under relatively severe conditions (8 MPa $CO_2$, 150 °C, 10 h), presumably via reaction of amine ($R_2NH$) with potassium carbamate ($R_2NCOOK$).[38] Such conditions are not pertinent to the current work. The isocyanate mechanism is likely to apply for the formation of open-chain di- or trisubstituted ureas, or *N*-substituted cyclic ureas, that is, whenever a primary amine is involved (Scheme 1, Mechanism A, Route 1 and Mechanism B, Route 1). However, as far as the formation of open-chain ureas is concerned, although less likely than the isocyanate route, the dehydration of disubstituted ammonium carbamate derived from primary amine or trisubstituted ammonium carbamate derived from mixed amines cannot be ruled out (Mechanism A, Route 2).

As for adsorbents containing ethylenediamine units such as Diamine, TRI, BPEI and LPEI, the intramolecular dehydration of the corresponding ammonium carbamate or carbamic acid (Scheme 1, Mechanism B, Route 2), leading to the formation of cyclic ureas is particularly favored. Lepaumier et al.[42] investigated the behavior of a series of ethylenediamines in the presence of $CO_2$ (2–5 mol amine/kg water, 2 MPa $CO_2$, 140 °C, 15 days). They reported that one of the main degradation pathways of such diamines was the formation of imidazolidinones even in the presence of water. Moreover, the deactivation was particularly fast for ethylenediamines with the general formula $R_1NH{-}CH_2{-}CH_2{-}NHR_2$. Further studies showed that diamines and triamines, capable of generating five- or six-membered rings, are particularly prone to deactivation.[44] Likewise, Seki et al.[45,46] found that *N,N′*-dimethylethylenediamine affords the corresponding 1,3-dimethyl-2-imidazolidinone in the presence of $CO_2$ (16 MPa, 200 °C), apparently catalyzed by amorphous silica.

One of the most intriguing findings in this work is that while secondary monoamines are exceedingly resistant to $CO_2$-induced deactivation, linear polyethyleneimine which comprises only secondary ethylenediamine units deactivates readily. This is in line with several literature reports showing the lack of reactivity of secondary monoamines,[31,41,42] and the high reactivity of ethylenediamine units, including secondary diamines.[43−46] If one of the two amine groups is primary in nature as in Diamine, the formation of the corresponding imidazolidinone may take place through the intermediacy of isocyanate (Scheme 1, Mechanism B, Route 1). However, if both amines are secondary, the deactivation must involve the intramolecular dehydration of the corresponding ammonium carbamate or the carbamic acid (Scheme 1, Mechanism B, Route 2). This mechanism applies to LPEI, and possibly to TRI and BPEI.

**Scheme 1. Proposed Mechanisms for $CO_2$-Induced Degradation of Supported Amines**



## 4. CONCLUSIONS

The effect of $CO_2$ under dry condition on mesoporous silica-containing amines was investigated using a wide variety of amines, including primary and secondary monoamines, mixed primary and secondary di- and triamines as well as different polyethylenimines. Except for secondary monoamines, all other materials were significantly deactivated in the presence of dry carbon dioxide under mild conditions via the formation of urea linkages at the expense of amine groups. In all cases, the nature of the urea species has been identified and different reaction pathways have been proposed, depending on the structure and nature of the amine-containing species. Materials containing primary amines are most likely to deactivate through the intermediacy of isocyanate followed by reaction with primary or secondary amine into di- and trisubstituted open-chain ureas or *N*-substituted imidazolidinones. As for materials containing ethylenediamine units with secondary amines, the formation of the corresponding *N,N′*-disubstituted imidazolidinones takes place through the dehydration of ammonium carbamate or carbamic acid.

It is conceivable that, using a humidified inert gas under relatively high temperature (100−200 °C), all or some $CO_2$-deactivated materials may be regenerated via urea hydrolysis. Nonetheless, this step would be extremely time and energy consuming. Therefore, every effort should be made to avoid such $CO_2$-induced deactivation by using feed and purge gases containing water vapor.

## ■ ASSOCIATED CONTENT

### Supporting Information

Structural properties of all supports and adsorbents. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

abdel.sayari@uottawa.ca

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The financial support of the Natural Science and Engineering Council of Canada (NSERC) and Carbon Management Canada is acknowledged. A.S. thanks the Federal Government for the Canada Research Chair in *Nanostructured Materials for Catalysis and Separation* (2001−2015).

## ■ REFERENCES

(1) Markewitz, P.; Kuckshinrichs, W.; Leitner, W.; Linssen, J.; Zapp, P.; Bongartz, R.; Schreibera, A.; Müller, T. E. *Energy Environ. Sci.* **2012**, *5*, 7281−7305.

(2) Harlick, P. J. E.; Sayari, A. *Ind. Eng. Chem. Res.* **2007**, *46*, 446−458.

(3) Hicks, J. C.; Drese, J. H.; Fauth, D. J.; Gray, M. L.; Genggeng, Q.; Jones, C. W. *J. Am. Chem. Soc.* **2008**, *130*, 2902−2903.

(4) Hiyoshi, N.; Yogo, K.; Yashima, T. *Microporous Mesoporous Mater.* **2005**, *84*, 357−365.

(5) Belmabkhout, Y.; Sayari, A. *Adsorption* **2009**, *15*, 318−128.

(6) Chang, F.-Y.; Chao, K.-J.; Cheng, H.-H.; Tan, C.-S. *Sep. Purif. Technol.* **2009**, *70*, 87−95.

(7) Xu, X. C.; Song, C. S.; Miller, B. G.; Scaroni, A. W. *Fuel Process. Technol.* **2005**, *86*, 1457−1472.

(8) Ma, X.; Wang, X.; Song, C. J. *J. Am. Chem. Soc.* **2009**, *131*, 5777−5783.

(9) (a) Chen, C.; Yang, S. T.; Ahn, W. S.; Ryoo, R. *Chem. Commun.* **2009**, 3627−3629. (b) Chen, C.; Son, W. J.; You, K. S.; Ahn, J. W.; Ahn, W. S. *Chem. Eng. J.* **2010**, *161*, 46−52.

(10) Qi, G.; Wang, Y.; Estevez, L.; Duan, X.; Anako, N.; Park, A. H. A.; Li, W.; Jones, C. W.; Giannelis, E. P. *Energy Environ. Sci.* **2011**, *4*, 444−452.

(11) Subagyono, D. J. N.; Liang, Z.; Knowles, G. P.; Chaffee, A. L. *Chem. Eng. Res. Des.* **2011**, *89*, 1647−1657.

(12) Ebner, A. D.; Gray, M. L.; Chisholm, N. G.; Black, Q. T.; Mumford, D. D.; Nicholson, M. A.; Ritter, J. A. *Ind. Eng. Chem. Res.* **2011**, *50*, 5634−5641.

(13) Chaikittisilp, W.; Khunsupat, R.; Chen, T. T.; Jones, C. W. *Ind. Eng. Chem. Res.* **2011**, *50*, 14203−14210.

(14) Heydari-Gorji, A.; Belmabkhout, Y.; Sayari, A. *Langmuir* **2011**, *27*, 12411−12416.

(15) Heydari-Gorji, A.; Sayari, A. *Chem. Eng. J.* **2011**, *173*, 72−79.

(16) Heydari-Gorji, A.; Yang, Y.; Sayari, A. *Energy Fuels* **2011**, *25*, 4206−4210.

(17) Goeppert, A.; Czaun, M.; May, R. B.; Prakash, G. K. S.; Olah, G. A.; Narayanan, S. R. *J. Am. Chem. Soc.* **2011**, *133*, 20164−20167.

(18) Wang, D.; Ma, X.; Sentorun-Shalaby, C.; Song, C. *Ind. Eng. Chem. Res.* **2012**, *51*, 3048−3057.

(19) Sayari, A.; Belmabkhout, Y.; Serna-Guerrero, R. *Chem. Eng. J.* **2011**, *171*, 760−774.

(20) Samanta, A.; Zhao, A.; Shimizu, G. K. H.; Sarkar, P.; Gupta, R. *Ind. Eng. Chem. Res.* **2011**, *51*, 1438−1463.

(21) Drage, T. C.; Snape, C. E.; Stevens, L. A.; Wood, J.; Wang, J.; Cooper, A. I.; Dawson, R.; Guo, X.; Satterley, C.; Irons, R. *J. Mater. Chem.* **2012**, *22*, 2815−2823.

(22) Choi, S.; Drese, J. H.; Jones, C. W. *ChemSusChem* **2009**, *2*, 796−854.

(23) (a) Belmabkhout, Y.; Heymans, N.; De Weireld, G.; Sayari, A. *Energy Fuels* **2011**, *25*, 1310−1315. (b) Belmabkhout, Y.; De Weireld, G.; Sayari, A. *Langmuir* **2009**, *25*, 13275−13278.

(24) Khatri, R. A.; Chuang, S. S. C.; Soong, Y.; Gray, M. *Energy Fuels* **2006**, *20*, 1514−1520.

(25) Bollini, P.; Choi, S.; Drese, J. H.; Jones, C. W. *Energy Fuels* **2011**, *25*, 2416−2425.

(26) Heydari-Gorji, A.; Belmabkhout, Y.; Sayari, A. *Microporous Mesoporous Mater.* **2011**, *145*, 145−149.

(27) Calleja, G.; Sanz, R.; Arencibia, A.; Sanz-Pérez, E. S. *Top. Catal.* **2011**, *54*, 135−145.

(28) Sayari, A.; Belmabkhout, Y. *J. Am. Chem. Soc.* **2010**, *132*, 6312−6314.

(29) Heydari-Gorji, A.; Sayari, A. *Ind. Eng. Chem. Res.* **2012**, *51*, 6887−6894.

(30) Drage, T. C.; Arenillas, A.; Smith, K. M.; Snape, C. E. *Microporous Mesoporous Mater.* **2008**, *116*, 504−512.

(31) Sayari, A.; Belmabkhout, Y.; Da'na, E. *Langmuir* **2012**, *28*, 4241−4247.

(32) Cokaja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8510−8537.

(33) Li, W.; Bollini, P.; Didas, S. A.; Choi, S.; Drese, J. H.; Jones, C. W. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3363−3372.

(34) Chaikittisilp, W.; Kim, H.-J.; Jones, C. W. *Energy Fuels* **2011**, *25*, 5528−5537.

(35) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024−6036.

(36) Sayari, A.; Han, B.-H.; Yang, Y. *J. Am. Chem. Soc.* **2004**, *126*, 14348−14349.

(37) (a) Slonim, I. Ya.; Alekseyeva, S. G.; Urman, Ya. G.; Arshava, B. M.; Aksel'rod, B. Ya.; Smirnova, L. N. *Polym. Sci. U.S.S.R.* **1977**, *19*, 920−936. (b) Nomura, K.; Hasegawa, Y.; Ishimoto, M.; Toyosaki, T.; Matsuda, H. *J. Org. Chem.* **1992**, *57*, 7339−7342. (c) Irsch, G.; Rademacher, P. *J. Mol. Struct.* **1990**, *222*, 265−263. (d) Kalinowski, H.-O.; Kessler, H. *Org. Magn. Reson.* **1974**, *6*, 305−312.

(38) Kong, D. L.; He, L. N.; Wang, J. Q. *Synlett* **2010**, *8*, 1276−1280.

(39) St. Pierre, T.; Geckle, M. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **1985**, *22*, 877−887.

(40) Harnagea, E. I.; Jagodzinski, P. W. *Vib. Spectrosc.* **1996**, *10*, 169−175.

(41) Wu, C.; Cheng, H.; Liu, R.; Wang, Q.; Hao, Y.; Yu, Y.; Zhao, F. *Green Chem.* **2010**, *12*, 1811−1816.

(42) Ion, A.; Parvulescu, V.; Jacobs, P.; De Vos, D. *Green Chem.* **2007**, *9*, 158−161.

(43) Lepaumier, H.; Picq, D.; Carrette, P. L. *Ind. Eng. Chem. Res.* **2009**, *48*, 9061−9067.

(44) Lepaumier, H.; Martin, S.; Picq, D.; Delfort, B.; Carette, P. L. *Ind. Eng. Chem. Res.* **2010**, *49*, 4553−4560.

(45) Seki, T.; Ikariya, T. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10073−10079.

(46) Seki, T.; Kokubo, Y.; Ichikawa, S.; Suzuki, T.; Kayaki, Y.; Ikariya, T. *Chem. Commun.* **2009**, 349−351.