Important Roles of Enthalpic and Entropic Contributions to CO$_2$ Capture from Simulated Flue Gas and Ambient Air Using Mesoporous Silica Grafted Amines

Mustafa A. Alkhabbaz,[†] Praveen Bollini,[†] Guo Shiou Foo, Carsten Sievers, and Christopher W. Jones*

School of Chemical & Bimolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, Georgia 30332, United States

Ⓢ *Supporting Information*

ABSTRACT: The measurement of isosteric heats of adsorption of silica supported amine materials in the low pressure range (0–0.1 bar) is critical for understanding the interactions between CO$_2$ and amine sites at low coverage and hence to the development of efficient amine adsorbents for CO$_2$ capture from flue gas and ambient air. Heats of adsorption for an array of silica-supported amine materials are experimentally measured at low coverage using a Calvet calorimeter equipped with a customized dosing manifold. In a series of 3-aminopropyl-functionalized silica materials, higher amine densities resulted in higher isosteric heats of adsorption, clearly showing that the density/proximity of amine sites can influence the amine efficiency of adsorbents. In a series of materials with fixed amine loading but different amine types, strongly basic primary and secondary amine materials are shown to have essentially identical heats of adsorption near 90 kJ/mol. However, the adsorption uptakes vary substantially as a function of CO$_2$ partial pressure for different primary and secondary amines, demonstrating that entropic contributions to adsorption may play a key role in adsorption at secondary amine sites, making adsorption at these sites less efficient at the low coverages that are important to the direct capture of CO$_2$ from ambient air. Thus, while primary amines are confirmed to be the most effective amine types for CO$_2$ capture from ambient air, this is not due to enhanced enthalpic contributions associated with primary amines over secondary amines, but may be due to unfavorable entropic factors associated with organization of the second alkyl chain on the secondary amine during CO$_2$ adsorption. Given this hypothesis, favorable entropic factors may be the main reason primary amine based adsorbents are more effective under air capture conditions.

The increasing level of CO$_2$ in the atmosphere is considered one of the main contributors to global climate change. Due to the impact of CO$_2$ emissions on the environment, recent efforts have focused on developing advanced materials and technologies that can reduce CO$_2$ emissions. Absorption in amine-based solutions, considered as the benchmark technology for postcombustion CO$_2$ capture, has many drawbacks, such as energy-intensive regeneration of the aqueous amine solutions, degradation of aqueous amines, and corrosion of process equipment.[1] Recently, adsorption-based technologies have attracted significant attention as a potentially more efficient alternative for CO$_2$ capture.[2−4] A large number of solid materials have been investigated for CO$_2$ capture, including zeolites,[5,6] activated carbons,[7,8] metal−organic frameworks,[9−11] and supported amine adsorbents,[12−17] among others.

Supported amine adsorbents have emerged as promising solids for CO$_2$ capture from point sources such as flue gas (5−15% CO$_2$) and for direct air capture[18−21] (ca. 400 ppm). This is due to their exceptional CO$_2$ adsorption capacities, high CO$_2$ selectivities, and their tolerance to water under conditions that are relevant to flue gas and ambient air.[2,17] While much of the research has focused on synthesizing adsorbents with enhanced CO$_2$ capacities, the molecular basis for CO$_2$ adsorption is not yet well developed, with most reports on the adsorption mechanism based primarily on *in situ* IR analyses.[22−24] In this regard, understanding and quantifying the strength of the interactions between CO$_2$ and amine sites is critical to the development of efficient amine adsorbents.

In an effort to gain insight into adsorption thermodynamics, several studies have reported estimated isosteric heats of CO$_2$ adsorption as a function of the amount of CO$_2$ adsorbed on supported amine adsorbents.[25−29] The reported heats of adsorption are typically calculated via the Clausius−Clapyeron equation using isotherm measurements (for example, using the Toth model[30−33]) at multiple temperatures. However, these values are not routinely compared to directly measured adsorption heats.

Only a few studies have reported directly measured isosteric heats of adsorption from calorimetric experiments. Knöfel et al.[34] reported heats of adsorption of CO$_2$ for silica functionalized with the diamine *N*-[3-(trimethoxysilyl)propyl]-ethylenediamine over a pressure range of 0−6 bar. Llewellyn et al. investigated CO$_2$ adsorption on supported amine adsorbents, reporting enthalpies of adsorption on 3-aminopropylsilane functionalized mesoporous silica and titania supports up to a pressure of 1 bar[35] and on amine functionalized mesoporous silica over a pressure range of 0−2.5 bar.[36] Also, the effect of impregnating zeolite 13X with monoethanolamine on the CO$_2$ adsorption enthalpy has been reported recently at a pressure up to 1 bar.[37]

These calorimetric isosteric heats of adsorption for supported amine materials were measured at pressures up to a few bars.

However, the CO_2 pressure region that is of interest to postcombustion CO_2 capture and direct air capture is below ca. 0.1 bar, a regime where few data exist, with only two data points below 0.01 bar of CO_2 published.[35,37] Especially for direct air capture purposes, understanding the thermodynamics at coverages approaching zero is critical to the generation of a fundamental understanding of CO_2-supported amine interactions, allowing for rational design of improved sorbents. In this work, we report experimentally measured calorimetric heats of adsorption of supported amine materials at ultralow CO_2 pressures (0−0.1 bar). The effect of amine density on the heats of adsorption is investigated using a series of 3-aminopropylsilyl functionalized silica adsorbents with different amine loadings. Furthermore, an array of aminosilane-grafted silica adsorbents with different amine structures is examined to study the effect of amine structure on the heats of adsorption of CO_2. The measured adsorption heats lead to some unexpected trends and offer insight into the design of effective adsorbents for direct air capture of carbon dioxide. A detailed description of the procedures for synthesis of adsorbents, material characterization, and calorimetry experiments can be found in the Supporting Information (SI).

To explore the impact of amine density on heats of adsorption, a series of materials was prepared by grafting 3-aminopropylsilyl groups (APS) onto a presynthesized mesoporous SBA-15 support with different APS loadings, with the obtained amine loadings varying from 0.87 to 1.87 mmol N/g. The isosteric heats of adsorption and adsorption isotherms are compared to those for bare SBA-15, as shown in Figure 1. The isosteric heat of adsorption for the material with the lowest amine loading (0.87 mmol N/g) is very similar to that of the bare SBA-15 support. Thus, even with a significant amount of primary amines on the

surface, if the loading is too low, relatively weak binding occurs, likely due to the low probability of paired amines being available to create alkylammonium carbamate species (vide infra). However, as the amine loading is increased, the isosteric heats of adsorption at a surface coverage close to zero increase significantly, with the adsorbent with the highest amine loading of 1.87 mmol N/g reaching an isosteric heat of adsorption of 92 kJ/mol at close to zero coverage.

There are several reports in the literature of an increase in the amine efficiency with increasing amine loading.[12,38] The increase in amine efficiency as a function of amine loading can be interpreted as a consequence of the proposed CO_2−amine reaction mechanism under dry conditions, where two amine groups are typically required to capture one molecule of CO_2, forming alkylammonium carbamates.[17,39] Hence, a higher density of amines on the support results in greater amine efficiency as well as stronger CO_2 binding. Interestingly, from the data in Figure 1, there is a threshold loading of amine groups, after which strong binding increases, with the threshold lying between 1.2 and 1.4 mmol amine/g using the support employed here. Similarly, at the highest loading of amines, with a relatively dense array of amine groups, productive amine−CO_2−amine reactions occur over a wider range of surface coverages, leading to higher heats of adsorption at elevated CO_2 coverages. This effect is demonstrated in terms of average amine spacing in Figure S5 in the SI. The heat of adsorption at zero coverage increases significantly once the average amine spacing reaches a value below ca. 11−12 Å, assuming all sites are equally spaced.[40] Given an amine footprint of ∼50 Å^2, which translates to the amine group being flexible enough to reach up to 4 Å away from its grafting location, amine groups are expected to be able to interact cooperatively to adsorb CO_2 at an amine spacing approaching 8 Å.[41] The enhancement in the heat of adsorption between 11 and 12 Å is therefore roughly consistent with the expected footprint of the grafted aminopropyl groups. The discrepancy may be ascribed to the tendency for amines to cluster during grafting,[42] and not be perfectly statistically distributed on the surface. It should be noted that the nature of the adsorbed CO_2 does not significantly change in materials with low and high amine loadings (1.2 and 1.87 mmol N/g), based on *in situ* FT-IR spectra collected at ultralow CO_2 pressures, which showed the presence of alkylammonium carbamate species on both materials (Figures S6 and S7).

There are several reported investigations of the difference of performance of primary vs secondary amines for CO_2 capture using adsorbents at the same amine loading. Zelenak et al.[43] investigated 3-aminopropyl (APS) and *n*-methyl-3-aminopropyl (MAPS) functionalized mesoporous SBA-12 adsorbents at 0.1 bar of CO_2 in N_2 and reported amine efficiencies for the APS adsorbents that were higher than those for the MAPS adsorbents. Another group reported amine efficiencies for APS functionalized silica that were 16% higher than those for MAPS functionalized silica at the same amine loadings, with measurements carried out at 1 bar of CO_2.[44] Didas et al.[33] reported amine efficiencies for APS and MAPS functionalized mesocellular foam silica with similar loadings at ultradilute conditions. In their report, they observed amine efficiencies for the APS adsorbent that were more than twice that of the MAPS adsorbent at 0.0004 bar, and about 1.4 times that of the MAPS materials at 0.1 bar. It was suggested that the higher amine efficiency for primary amines was a consequence of higher heats of adsorption for primary amines than secondary amines, and the adsorption heats were estimated using the Toth equation to model isotherms at
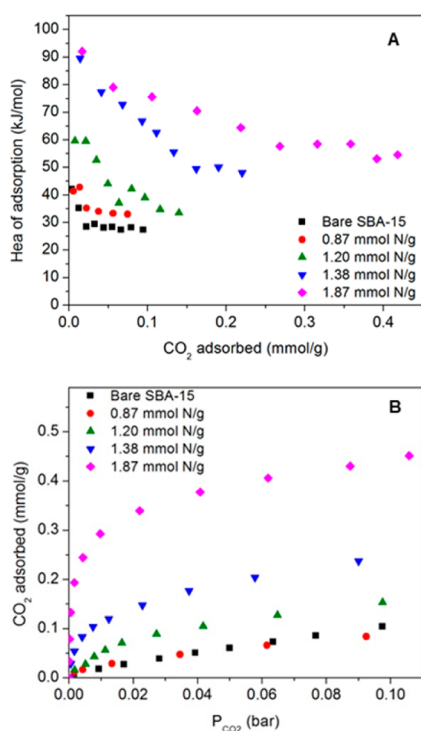

Figure 1. (A) Isosteric heats of adsorption as a function of surface coverage and (B) adsorption isotherm for aminopropylsilyl functionalized SBA-15 adsorbents at different amine loadings. See SI for discussion of adsorption capacities.

different temperatures. Apart from the comparison of APS to MAPS materials, the impact of using different amine structures at a fixed loading on the efficiency of amine adsorbents is not very well studied.

To this end, a series of supported amine adsorbents with different alkyl groups attached to the nitrogen atom in an aminopropylsilyl framework were synthesized to investigate the effect of amine structure on CO_2 adsorption efficiency via direct isosteric heat of adsorption measurements. In addition to the traditional 3-aminopropylsilyl (APS) material used, structures where the amine was substituted with methyl, n-butyl, cyclohexyl, and phenyl groups were prepared and tested as well. The series included APS, MAPS, NBAPS, CHAPS, and PHAPS materials respectively, as shown in Figure 2.
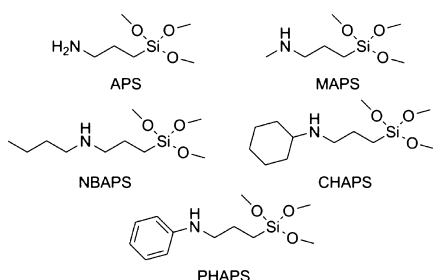

Figure 2. Different amine adsorbent structures used to study the effect of amine structure.

Figure 3 shows the measured isosteric heats of adsorption for the amine structures shown above in addition to the bare support. The initial heats of adsorption for the APS, MAPS, and NBAPS materials fall in the same range of ~86−92 kJ/mol. This observation was surprising, as it is known that primary amines are
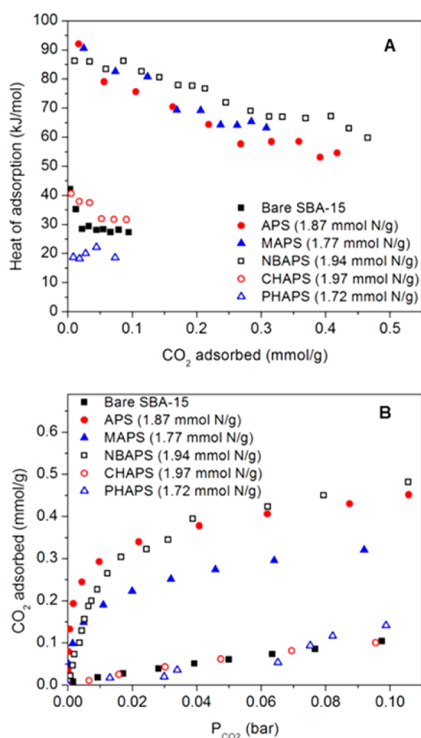

Figure 3. (A) Isosteric heats of adsorption as a function of surface coverage and (B) adsorption isotherm for amine functionalized SBA-15 with different amine structures.

most effective under air capture conditions and this has been assumed to be due to a higher isosteric heat of adsorption for these materials,[33] as noted above. However, these results show that some secondary amines have essentially identical heats, even in a pressure range where the amounts of adsorbed CO_2 were quite different.

Interestingly, the isosteric heat of adsorption for the NBAPS material starts lower than the APS materials but ends ~6 kJ/mol (well above instrumental error range; see SI) higher than the APS materials at the surface coverage corresponding to 0.1 bar of CO_2. This isosteric heat trend of the NBAPS material correlates well with the observed adsorption isotherm, which shows a (slightly) lower performance compared to the APS and MAPS materials at ultralow pressures, and a better performance at higher pressures. Surface area analysis showed that the NBAPS materials had a surface area of 252 m^2/g, which is lower than that of APS and MAPS materials with 295 and 326 m^2/g, respectively. Hence, the enhanced performance of the NBAPS materials at higher pressure is not likely a result of the differences in the amount of CO_2 physisorbed. It may be that the observed performance of NBAPS at higher pressure is a result of better amine spacing due to the bulkier n-butyl group in this material.

The isosteric heats of adsorption of the CHAPS material are lower than the heats for the APS, MAPS, and NBAPS materials and close to the bare SBA-15 support, starting about 50 kJ/mol lower than the APS materials at close to zero coverage. This can be a result of the significant contribution of CO_2 physisorption onto the support compared to the overall amount of CO_2 adsorbed. It is anticipated that the steric constraints associated with the cyclohexyl group disfavor chemisorption at the amine site. The PHAPS material showed the lowest heat of adsorption of all materials investigated in this study, even lower than the bare SBA-15 support. This is likely due to the electron-withdrawing phenyl group resulting in a reduced basicity of the amine group, making chemisorption at amine sites improbable, while the large organic groups simultaneously block the few remaining surface silanols that might bind the CO_2 via physisorption.

The isosteric heats of adsorption of the APS and MAPS materials showed similar isosteric heats as a function of coverage, which is markedly different from what was estimated from previous studies that applied the Clausius−Clapeyron equation to isotherms at multiple temperatures as described by the Toth model.[33] As also noted above, these two materials have significantly different CO_2 uptakes at ultralow pressures (Figure 1) and different amine efficiencies. The new calorimetric results reported here suggest that the observed trend in the literature of higher amine efficiencies for primary amine (APS) adsorbents compared to secondary amine (MAPS) adsorbents are not due to enthalpic factors as originally postulated[33] but instead may result from entropic factors associated with the extra chain attached to the amine site (Me in MAPS and n-Bu in NBAPS). Thus, this work shows that significant errors in the heats of adsorption can be obtained via the methodology most commonly used in the literature to estimate adsorption heats, application of the Clausius−Clapeyron equation to multi-temperature iso-therm data. For accurate assessment of adsorption enthalpies, direct measurement of adsorption heats is thus advocated.

In summary, isosteric heats of adsorption were experimentally measured for a series of supported amine adsorbents in which the impact of amine density and amine structure was investigated at low CO_2 pressures and surface coverages relevant to CO_2 capture from flue gas and ambient air. Higher amine loadings resulted in higher isosteric heats of adsorption, which indicated that amine

density can influence the heat of adsorption and the amine efficiency of the adsorbents, likely by promoting effective amine−CO_2−amine interactions in the formation of alkylammonium carbamates. A significant jump in the heat of adsorption occurred at a threshold amine loading between 1.2 and 1.4 mmol amine/g over this support material, a coverage whereby productive amine−amine interactions start to readily occur, promoting adsorption by formation of alkylammonium carbamate species.

Functionalizing amine sites with bulky or electron-withdrawing groups resulted in very low adsorption heats and amine efficiencies. Among the materials composed of only linear alkyl chains attached to the amine sites, including APS, MAPS, and NBAPS materials, the measured heats of adsorption at coverages approaching zero were all similar, yet the primary amine material, APS, had significantly higher CO_2 uptake at ultralow pressures compared to the secondary amine containing materials, which suggests that entropic factors are important to consider for the design of amine adsorbents for CO_2 capture from ambient air with enhanced efficiencies (see SI for discussion). Primary amine containing materials remain most effective for CO_2 adsorption under air capture conditions, but not due to strictly enthalpic factors, as was hypothesized previously.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials synthesis; materials characterization; calorimeter experimental setup; calorimeter dosing procedure; calorimeter measurements validation; thermogravimetric analysis curves; nitrogen physisorption isotherms, average amine spacing, and in situ FT-IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
cjones@chbe.gatech.edu
Author Contributions
[†]M.A.A. and P.B. contributed equally.
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Bishnoi, S.; Rochelle, G. T. *Chem. Eng. Sci.* **2000**, *55*, 5531.
(2) Choi, S.; Drese, J. H.; Jones, C. W. *ChemSusChem* **2009**, *2*, 796.
(3) D'Alessandro, D. M.; Smit, B.; Long, J. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6058.
(4) Hedin, N.; Chen, L.; Laaksonen, A. *Nanoscale* **2010**, *2*, 1819.
(5) Pham, T. D.; Liu, Q.; Lobo, R. F. *Langmuir* **2013**, *29*, 832.
(6) Zhang, J.; Singh, R.; Webley, P. A. *Microporous Mesoporous Mater.* **2008**, *111*, 478.
(7) Drage, T. C.; Blackman, J. M.; Pevida, C.; Snape, C. E. *Energy Fuels* **2009**, *23*, 2790.
(8) Sethia, G.; Sayari, A. *Energy Fuels* **2014**, *28*, 2727.
(9) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2011**, *112*, 724.
(10) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 10870.
(11) Keskin, S.; van Heest, T. M.; Sholl, D. S. *ChemSusChem* **2010**, *3*, 879.
(12) Hiyoshi, N.; Yogo, K.; Yashima, T. *Microporous Mesoporous Mater.* **2005**, *84*, 357.
(13) Khatri, R. A.; Chuang, S. S. C.; Soong, Y.; Gray, M. *Energy Fuels* **2006**, *20*, 1514.
(14) Hicks, J. C.; Drese, J. H.; Fauth, D. J.; Gray, M. L.; Qi, G.; Jones, C. W. *J. Am. Chem. Soc.* **2008**, *130*, 2902.
(15) Belmabkhout, Y.; Sayari, A. *Energy Fuels* **2010**, *24*, 5273.
(16) Choi, S.; Drese, J. H.; Eisenberger, P. M.; Jones, C. W. *Environ. Sci. Technol.* **2011**, *45*, 2420.
(17) Bollini, P.; Didas, S. A.; Jones, C. W. *J. Mater. Chem.* **2011**, *21*, 15100.
(18) Belmabkhout, Y.; Serna-Guerrero, R.; Sayari, A. *Chem. Eng. Sci.* **2010**, *65*, 3695.
(19) Jones, C. W. *Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 31.
(20) Choi, S.; Drese, J. H.; Eisenberger, P. M.; Jones, C. W. *Environ. Sci. Technol.* **2011**, *45*, 2420.
(21) Gebald, C.; Wurzbacher, J. A.; Tingaut, P.; Zimmermann, T.; Steinfeld, A. *Environ. Sci. Technol.* **2011**, *45*, 9101.
(22) Bacsik, Z.; Atluri, R.; Garcia-Bennett, A. E.; Hedin, N. *Langmuir* **2010**, *26*, 10013.
(23) Danon, A.; Stair, P. C.; Weitz, E. *J. Phys. Chem. C* **2011**, *115*, 11540.
(24) Srikanth, C. S.; Chuang, S. S. C. *J. Phys. Chem. C* **2013**, *117*, 9196.
(25) Leal, O.; Bolívar, C.; Ovalles, C.; García, J. J.; Espidel, Y. *Inorg. Chim. Acta* **1995**, *240*, 183.
(26) Zukal, A.; Jagiello, J.; Mayerová, J.; Čejka, J. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15468.
(27) Wang, L.; Yang, R. T. *J. Phys. Chem. C* **2011**, *115*, 21264.
(28) Belmabkhout, Y.; Sayari, A. *Adsorption* **2009**, *15*, 318.
(29) Watabe, T.; Yogo, K. *Sep. Purif. Technol.* **2013**, *120*, 20.
(30) Serna-Guerrero, R.; Belmabkhout, Y.; Sayari, A. *Chem. Eng. J.* **2010**, *161*, 173.
(31) Bollini, P.; Brunelli, N. A.; Didas, S. A.; Jones, C. W. *Ind. Eng. Chem. Res.* **2012**, *51*, 15145.
(32) Bollini, P.; Brunelli, N. A.; Didas, S. A.; Jones, C. W. *Ind. Eng. Chem. Res.* **2012**, *51*, 15153.
(33) Didas, S. A.; Kulkarni, A. R.; Sholl, D. S.; Jones, C. W. *ChemSusChem* **2012**, *5*, 2058.
(34) Knöfel, C.; Descarpentries, J.; Benzaouia, A.; Zeleňák, V.; Mornet, S.; Llewellyn, P. L.; Hornebecq, V. *Microporous Mesoporous Mater.* **2007**, *99*, 79.
(35) Knöfel, C.; Martin, C.; Hornebecq, V.; Llewellyn, P. L. *J. Phys. Chem. C* **2009**, *113*, 21726.
(36) Mello, M. R.; Phanon, D.; Silveira, G. Q.; Llewellyn, P. L.; Ronconi, C. M. *Microporous Mesoporous Mater.* **2011**, *143*, 174.
(37) Da Silva, F. W. M.; Maia, D. A. S.; Oliveira, R. S.; Moreno-Piraján, J. C.; Sapag, K.; Cavalcante, C. L.; Zgrablich, G.; Azevedo, D. C. S. *Can. J. Chem. Eng.* **2012**, *90*, 1372.
(38) Harlick, P. J. E.; Sayari, A. *Ind. Eng. Chem. Res.* **2006**, *45*, 3248.
(39) Caplow, M. *J. Am. Chem. Soc.* **1968**, *90*, 6795.
(40) An average amine spacing of roughly 18 Å was reported to be required for cooperative CO_2 uptake for an aminopropyl derived material in: Young, P. D.; Notestein, J. M. *ChemSusChem* **2011**, *4*, 1671.
(41) Vansant, E. F.; Van Der Voort, P.; Vrancken, K. C. *Characterization and Chemical Modification of the Silica Surface*; Elsevier: Amsterdam, 1995.
(42) Hicks, J. C.; Dabestani, R.; Buchanan, A. C.; Jones, C. W. *Chem. Mater.* **2006**, *18*, 5022.
(43) Zelenak, V.; Halamova, D.; Gaberova, L.; Bloch, E.; Llewellyn, P. *Microporous Mesoporous Mater.* **2008**, *116*, 358.
(44) Ko, Y. G.; Shin, S. S.; Choi, U. S. *J. Colloid Interface Sci.* **2011**, *361*, 594.