Tubular Clay Nano-Straws in Ordered Mesoporous Particles Create Hierarchical Porosities Leading to Improved CO₂ Uptake

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ABSTRACT: The use of solid adsorbents for CO₂ capture is of importance in the development of technologies to remove this greenhouse gas. High surface area mesoporous materials are used to encapsulate or functionalize amines that selectively capture CO₂. The MCM-41 class of hexagonally ordered mesoporous silicas have surface areas between 1000 and 1500 m²/g, which in principle allows a significant degree of capture when amines such as polyethyleneimine (PEI) are encapsulated within the pores and occupy the entire surface area of the materials. However, the tight 3 nm pore channels of MCM-41 create a challenge to the infiltration of PEI throughout the pore volume, resulting in much lower CO₂ uptake at high PEI concentrations. This work describes the introduction of clay nanotubes (halloysite) with an inner diameter of 15−30 nm into MCM-41 pellets to mitigate such diffusional restrictions. The introduction of the nanotubes is through a one-step ship-in-a-bottle approach to synthesis in an aerosol-assisted system where MCM-41 is synthesized in droplets containing the halloysite. The morphology of the composite material is such that several nanotubes extend from the interior and protrude through the surface of the pellet like straws. These ceramic nanotubes are 0.5−2 μm in length, and their lumen diameter ranges from 15 to 30 nm, thus providing an improved entry pathway for molecules to access the interior of the MCM-41 pellets. The concept is used to enhance PEI loading in MCM-41, which leads to a significant increase in CO₂ uptake levels. MCM-41 composites with halloysite nano-straws (MCM-41/HNT) show a doubling of CO₂ uptake levels (7.1 wt %) and uptake kinetics (k = 0.11 s⁻¹) in comparison to MCM-41 sorbents (3.9 wt % and k = 0.05 s⁻¹) at 50 wt % PEI loading. This indicates the potential validity of the nano-straws to improve access to the interior of MCM-41, thus coupling enhanced molecular transport with a high surface area material. The generality of the concept indicates further applications to adsorption and catalysis.

INTRODUCTION

The adsorption of CO₂ onto amine-modified solid adsorbents is of intense interest as an alternative to the liquid amine solution absorption process. In contrast to solution-based absorption processes, solid adsorbents require a significantly lower energy input to regenerate the adsorbent as energy is not wasted to heat the solvent. In amine-containing solid adsorbent systems, CO₂ reacts easily and reversibly with the amine functional groups to form carbamates or bicarbonates under dry and humid conditions, respectively. Studies have shown that amine-modified solid materials such as mesoporous silicas, zeolites, activated carbons, polymeric fibers, nanoclays, and metal organic frameworks are effective in the capture of CO₂ from pure CO₂ streams, ambient air, or simulated flue gases under a wide range of conditions. Solid adsorbent materials used in this technology are typically highly porous with large surface areas. The adsorbents for CO₂
capture are prepared by infiltrating the pores of the solid materials with polymeric amine macromolecules such as polyethyleneimine (PEI)\textsuperscript{12} or by chemically grafting amine functional groups onto the surfaces and pores of the solid materials.\textsuperscript{13}

Of interest as a solid adsorbent is the ordered mesoporous silica (OMS) MCM-41 that has gained a wide range of applications in catalysis,\textsuperscript{14} molecular sorption,\textsuperscript{15} drug delivery,\textsuperscript{16} and separation processes.\textsuperscript{17} MCM-41 is typically synthesized via sol−gel hydrothermal synthesis by introducing a silicate source and a cationic templating surfactant.\textsuperscript{18} MCM-41 has a highly ordered hexagonal pore structure with pore size ranging from 2 to 4 nm, a pore volume of 0.25 to 0.75 cm$^3$/g, and a high surface area ranging from 1500 to 3000 m$^2$/g.\textsuperscript{19} MCM-41 has been proposed as a good candidate for CO$_2$ capture due to its facile synthesis, pore volume, high surface area, and ease of modification with amine-containing molecules.\textsuperscript{16} In a recent and relevant work, Mukherjee and co-workers\textsuperscript{22} have shown that MCM-41 adsorbent for CO$_2$ capture can be prepared by infiltrating the mesopores with amine-containing molecules such as monoethanolamine, benzylamine, and N-(2-aminoethyl) ethanolamine through a facile wet impregnation process.

While amine-infiltrated MCM-41 is a promising solid sorbent for CO$_2$ capture, the literature indicates that the CO$_2$ capture efficiency declines at higher loading concentrations of the amine (typically above 30 wt %).\textsuperscript{12} This phenomenon is especially pronounced with MCM-41 sorbents loaded with viscous polymeric amines such as PEI that have difficulty infiltrating the tight pores of MCM-41, due to the fact that the amine dimensions are comparable to the pore dimensions of MCM-41. We do this through the introduction of ceramic nano-straws that allow access to the interior of the particle, as shown schematically in Figure 1 (bottom). The procedure is based on a one-step aerosol-assisted method using the remarkable process developed by Lu and co-workers\textsuperscript{20} where material synthesis in the confined environment of a droplet using a silica source (tetraethyl orthosilicate, TEOS) and a templating agent (cetyltrimethylammonium bromide, CTAB) leads to the facile formation of MCM-41. The variation we introduce is the incorporation of halloysite nanotubes (HNT) into the precursor solution, where the nanotubes become integrated into the MCM-41, as shown in Figure 1. HNTs are naturally occurring aluminosilicate (Al$_2$(OH)$_3$Si$_2$O$_5$·nH$_2$O) clay minerals having a hollow tubular morphology. The lumen of HNT is made up of octahedrally structured Al−OH with a net positive charge, while the external surface is negatively charged with a Si−O−Si tetrahedral structure.\textsuperscript{21} The length of HNTs is 0.5 to 2 μm, external diameter is 50−80 nm, and lumen diameter ranges from 15 to 30 nm (Figure S2). The lumen of HNTs provides ample volume for the loading and release of guest molecules, enabling applications in drug delivery, corrosion inhibition,\textsuperscript{26} surfactant delivery for oil spill remediation,\textsuperscript{27,28} and oil recovery.\textsuperscript{29} Halloysite nanoclays have also been studied as a solid adsorbent for amine modification and CO$_2$ capture.\textsuperscript{8,5} In the work by Cai and co-workers,\textsuperscript{9} HNTs loaded with PEI was
shown to be a stable adsorbent for CO$_2$ capture with an optimum capacity of about 54.8 mg/g$_{\text{adsorbent}}$ at 35 wt % PEI loading, but the CO$_2$ capture capacity declined above 35 wt % PEI loading, which was attributed to the saturation of the halloysite lumen by PEI, causing restrictions to CO$_2$ diffusion.

We have thus conceptualized a ship-in-a-bottle process where MCM-41 synthesis in the droplet immobilizes HNT and forms the nano-straws for entry to the interior of the ordered mesoporous matrix. The basis of our hypothesis lies in the fact that the lumen diameter of HNTs (15–30 nm) is significantly larger than the 2–4 nm pores of MCM-41. Additionally, HNT straws traverse from the exterior to the interior of the MCM-41 particles, allowing direct access to the interior. The integration of HNTs in MCM-41 is a facile and scalable synthesis route for collection on the filter. The schematic is adapted from Su and co-workers.24,32

**EXPERIMENTAL SECTION**

**Materials.** TEOS (98%), Cetyltrimethylammonium bromide (CTAB, 95%), and hydrochloric acid (HCl, 37%) were purchased from Sigma-Aldrich. Branched PEI (600 $M_w$) was purchased from Alfa Aesar. The above chemicals were used without any modifications. South Australian Camel Lake (CLA) HNTs$^{30}$ were obtained as a gift from John Keeling (Department of State Development—Geological Survey, South Australia) and was purified to remove quartz and salt impurity using a previously reported technique outlined in the Supporting Information section.$^{31}$ Deionized (DI) water with a resistance of 18.2 MΩ was obtained from an Elga water purification system (Medica DV25).

**Synthesis of MCM-41 and MCM-41/HNT Composite Particles.** MCM-41 spherical particles were synthesized using the previously reported aerosol-assisted technique with slight modifications.$^{24,32}$ Briefly, 1.5 g of CTAB surfactant was dissolved in 20 mL ethanol (200 proof) in a vial. TEOS (4.5 mL) was then added to the surfactant solution slowly under continuous magnetic stirring. Then, 3 mL of 0.1 M HCl was added, and the solution was left to stir at room temperature for 10 min. This precursor solution was then transferred into a nebulizer (Micro Mist, Teleflex Inc., 1 mm jet hole diameter), where it was atomized by N$_2$ gas (2.5 L/min) into fine droplets. The droplet mist was carried into the heating chamber, where the hydrolysis and condensation of TEOS to silica took place rapidly, as illustrated in Figure 2. The heating chamber was a tubular furnace with a length of 76 cm and internal diameter of 5 cm operating isothermally at 400 °C. A filter paper (Merck Millipore Ltd., pore size = 0.22 μm) was used to collect the dried particles at the end of the furnace. The filtration setup was set at a temperature of 80 °C using heating coils to avoid condensation of moisture. The dried particles were collected and calcined in air at 550 °C for 8 h at a heating rate of 5 °C/min to remove the CTAB template. The preparation of MCM-41/HNT (M30H) composite particles followed the same methods as in MCM-41 except that 0.52 g of HNT particles was first dispersed evenly in 20 mL ethanol using a bath sonicator (VWR, B2500A-MTH) prior to the addition of CTAB, TEOS, and HCl as described above. The resulting slurry was left to stir at room temperature for 10 min before transferring it into the nebulizer for aerosolization. The composite MCM-41/HNT materials are hereby labeled as M30H.

**Loading of MCM-41 and MCM-41/HNT (M30H) with PEI.** MCM-41 and MCM-41/HNT (M30H) particles were loaded with branched PEI (600 $M_w$) by simple vacuum infiltration.$^{12}$ To achieve 50 wt % PEI loading, 250 mg PEI was dissolved in 6 mL 200 proof ethanol followed by the addition of 250 mg of either MCM-41 or M30H particles. The particles were dispersed in the PEI solution via bath sonication (VWR, B2500A-MTH) for 10 min followed by magnetic stirring for 15 h at room temperature. The slurry was transferred into a round bottom flask and hooked up to a rotavap (Buchi R-20S) rotating at 50 rpm and with a heating bath set at 60 °C. Vacuum suction (100 mbar) was applied to improve the loading of the PEI into the pores of the particles and to evaporate off the ethanol solvent. The dried sorbent was then
collected and stored for analysis. 10–40 wt % PEI-loaded sorbents were also prepared using the same technique by adjusting the mass ratio of PEI to solid particles of MCM-41 or M30H particles.

**Characterization of Composite Particles.** The morphology of the synthesized MCM-41 and M30H materials was visualized using scanning electron microscopy (SEM; Hitachi S-4800 field emission scanning electron microscope operated at 3 kV) and transmission electron microscopy (TEM; FEI Tecnai G2 F30 twin transmission electron microscope operated at 300 kV). Powder X-ray diffraction was carried out to obtain structural information about the materials using a Rigaku Miniflex II X-ray diffractometer having a Cu Kα X-ray source with a wavelength of 1.5418 Å. The small-angle scan was conducted from 2θ = 1.5 to 7°. Surface area analysis was obtained via a nitrogen gas sorption and desorption analyzer (Micromeritics, ASAP 2010). The surface area was obtained using the Brunauer—Emmett—Teller (BET) method. The amounts of PEI loaded onto each sorbent was quantified using thermogravimetric analysis (TGA; TA Instruments Q500).

**CO₂ Capture Analysis.** The CO₂ adsorption capacities of the MCM-41 and M30H sorbents pre-loaded with branched PEI were measured using the well-known TGA technique (TA Instruments Q500). Branched PEI (structure shown in Figure S1) was selected because it possesses a high composition of primary and secondary amines, which have been shown to have better CO₂ capture capacity from dry CO₂ streams as they readily form zwitterionic carbamates unlike tertiary amines that require hydrated conditions for the formation of bicarbonates. For each measurement, about 10 mg PEI-loaded solid sorbent was added onto the TGA platinum pan. The sample was first heated at 5 °C/min to 105 °C and held for 1 h under the flow of N₂ gas to remove any pre-adsorbed moisture or gases. Then, the temperature was lowered to 75 °C, after which the inlet gas was switched to pure dry CO₂ flowing at 90 mL/min for 2 h to allow for CO₂ adsorption. The mass of CO₂ adsorbed was obtained from the difference between the mass of the adsorbent before and after the introduction of CO₂ gas.

### RESULTS AND DISCUSSION

**Synthesis and Material Characterization.** The aerosol-assisted hydrothermal sol–gel synthesis technique is a facile process to synthesize spherical OMS particles such as MCM-41. In this process, precursor solutions containing an organic silicate source and cationic templating surfactants are aerosolized through a nebulizer whose orifice allows for the transport of fine droplet mist. These droplets are carried through a tubular furnace, where hydrolysis and condensation reaction occur rapidly in the confined volume of each droplet, enabling the formation of spherical silica particles within a short residence time (Figure 2). Post-synthesis calcination removes the templating surfactant, leaving an OMS particle, as demonstrated by Lu and co-workers in their landmark paper.

Figure 3a(i) shows an SEM image of MCM-41 particles synthesized via the aerosol-assisted process. The intrinsic nature of the aerosol process results in spherical particles that are polydisperse in size and the sizes of these MCM-41 particles range from about 50 nm to ∼2 µm. Figure 3a(ii) is a high-resolution SEM image of bare MCM-41 particles where the smooth surface morphology of MCM-41 particles is noted. The TEM image in Figure 3b(i) further provides a detailed visualization of the spherical morphology of these MCM-41 particles. Figure 3b(ii) is a high-resolution TEM image with a clear visualization of ordered mesopores. As we note, these are control samples and we simply reproduce results first reported by Lu et al.

Composite particles of MCM-41 and HNT denoted as M30H were obtained using the same synthesis procedure as that for MCM-41 with the addition of 30 wt % solid particles of HNTs dispersed into the MCM-41 precursor solution to form a slurry. HNTs used in this synthesis have lengths ranging from about 500 nm to 2 µm and external diameter of 60–80 nm, as shown in the TEM images of Figure S2. The 1 mm orifice size of the aerosol nebulizer is much larger than the dimensions of individual HNTs and allows multiple HNTs to be entrained in the MCM-41 precursor containing droplets upon aerosolization. During passage through the heated furnace zone, the HNT particles in the precursor droplets become immobilized as silica is formed. Electron microscopy images in Figure 4 reveal the morphology of the resulting particles and orientation of HNTs in the composite. In the SEM image of Figure 4a(i), we observe the formation of much larger particles compared to those of bare MCM-41 as we have particles up to 5 µm in diameter. The higher resolution SEM image in Figure 4a(ii) further reveals the uneven surface morphology of these M30H particles, and we can visualize multiple halloysite tubes sticking through the surface of the silica particles (indicated with arrows). Additionally, small satellite particles are seen, and these are MCM-41 particles without the incorporation of HNT. TEM images in Figure 4b(i) confirm that the surface features observed from the SEM images are indeed HNTs that extend from the interior and protrude through the surface of the silica particles like “straws.” The high-resolution TEM images in Figure 4b(ii) provide a visualization of an HNT piercing through the MCM-41 particle. In this image, we observe that the ordered mesoporous structure and the distinct tubular morphology of the HNT is preserved and the hollow lumen of the HNT is visible.

We also see a concave meniscus formed by MCM-41 around the exterior of the HNTs. This is due to the nucleation of MCM-41 that is formed upon adsorption of CTAB on the anionic external surface of the HNTs with a remnant film that
is left as the evaporating solvent front recedes inward. Figure 4b(ii) again clearly shows the MCM-41 structure of the small satellite particles that do not contain any HNT.

Figure 5a shows the small-angle X-ray diffraction pattern for the synthesized MCM-41 particles indicating the primary (100) diffraction peak at 2θ = 2.9° corresponding to a d-spacing of 3 nm. Higher order (101) and (200) diffraction peaks are seen at 2θ = 5.0 and 5.8°, respectively, confirming the long-range hexagonal order of the mesopores, which is characteristic of MCM-41-type mesoporous silicas. HNTs do not show any diffraction peaks in the small-angle range. X-ray diffraction pattern for the MCM-41/HNT (M30H) composite shows the characteristic MCM-41 (100) primary diffraction peak at 2θ = 2.6° (d = 3.4 nm), which is a slight shift to the left with respect to that of the bare MCM-41 and may have resulted from a strain in the MCM-41 matrix due to the incorporation of HNTs. Higher order (101) and (200) diffraction peaks at 2θ = 4.5 and 5.3°, respectively, confirm that the mesoporous silica formed maintains the hexagonal structural characteristics of MCM-41. BET surface area analysis of Figure 5b and Table 1 shows that MCM-41 has a high surface area as expected with a measured value of 1430 m²/g. The M30H composite maintains a high surface area similar to that of MCM-41 with a measured value of 1042 m²/g, which is essentially a weighted average based on the ratios of MCM-41 to HNT in the composite given the low surface area of HNTs (47 m²/g).

The electron microscopy imaging, XRD, and BET characterization data of Figures 2 and 3 confirm that M30H particles synthesized using the aerosol technique are composites of high surface area MCM-41 with 3 nm pores that have multiple HNTs protruding through the surface of the MCM-41 pellets, a term that we refer to as nano-straws based on the tubular morphology. Figure 6a,b shows cut-section TEMs of MCM-41 and M30H particles, respectively, where there is a clear distinction in the images. In Figure 6a(i), the lines seen are artifacts of the sectioning procedure and represent unavoidable glancing off of the diamond sectioning knife, besides which the internal surface of the MCM-41 is mostly uniform (Figure 6a(ii)). The cut-section TEM image of the M30H particles (Figure 6b(i)) shows multiple HNT tubes in a particle, some lying approximately parallel to the cut section (indicated by white arrows) and others lying approximately orthogonal (indicated by yellow arrows). The orthogonal sections are informative as they clearly show the lumen and indicate the strong possibility that the lumen is clear after synthesis of the composite. We expect an electrostatic repulsion between the cationic CTAB micelles carrying the nonpolar TEOS in the micellar core and the lumen of HNT, which is also positively charged due to the presence of octahedrally structured Al-OH. Capillary imbition of these micelles without adsorption to the lumen should therefore keep the lumen free of silica formation. Figure 6b(ii) is a high-resolution TEM image that visualizes the hollow lumen of the halloysites from the orthogonal sections of multiple HNTs in the composite M30H particle.

![Figure 4](image_url)

**Figure 4.** (a) SEM and (b) TEM showing the morphology of spherical mesoporous MCM-41/HNT (M30H) particles synthesized using the aerosol-assisted synthesis technique. Multiple HNTs are seen sticking into individual mesoporous silica particles like straws.

![Figure 5](image_url)

**Figure 5.** (a) X-ray diffraction patterns and (b) BET N₂ adsorption isotherm for HNTs, MCM-41, and MCM-41/HNT (M30H).

| sample          | BET surface area (m²/g) | total pore volume (cm³/g) | avg. pore diameter a (nm) |
|-----------------|-------------------------|--------------------------|--------------------------|
| MCM-41          | 1430                    | 0.84                     | 2.1                      |
| HNT             | 47                      | 0.22                     | 15.1                     |
| MCM-41/HNT (M30H) | 1042                   | 0.64                     | 2.9                      |

**Table 1. BET Surface Area Analysis Results**

[a] BJH desorption average pore diameter.
**PEI Loading and CO₂ Adsorption Studies.** As proof of concept that the incorporation of HNT nano-straws into MCM-41 pellets has the potential to enhance the loading and adsorption of molecules into the interior mesopores of the large particles, we measured the adsorption of CO₂ onto PEI pre-loaded into the MCM-41 or M30H particles. Under ambient conditions, the capture of CO₂ by amine-modified solid adsorbents occurs predominantly via chemisorption following the mechanisms shown in Scheme 1. Thus, in dry environments, carbamates are formed, while humid environments lead to the formation of bicarbonates.

**Scheme 1. Mechanism for CO₂ Capture by Surface-Bonded Amines under (a) Dry Conditions to Form Carbamate and (b) Humid Conditions to Form Bicarbonate**

\[
q_t = q_e (1 - e^{-kt})
\]

where \(q_e\) is the equilibrium adsorption capacity and \(q_t\) is the instantaneous adsorption capacity at time \(t\). The adsorption rate constant of \(k = 0.11 \text{ s}^{-1}\) obtained for the 50% PEI-M30H sorbent is 2.2 times greater than the corresponding value for the 50% PEI-MCM-41 sorbent \(k = 0.05 \text{ s}^{-1}\). This shows evidence of a much slower amine encounter rate in the 50% PEI-MCM-41 sorbent when compared to the 50% PEI-M30H sorbent. Again, we posit that this is due to the presence of surface PEI on the MCM-41 sorbent, which provides restrictions to transport into the porous MCM-41, as shown in the schematic of Figure 1. This is understandable considering that the branched PEI having a maximum longitudinal length of 2.1 nm and transverse length of 1.4 nm will have difficulty fully accessing the 3 nm pores of the MCM-41.

Figure 7a shows photographic images of MCM-41 and M30H adsorbents each loaded with 50 wt % PEI. For the MCM-41 sorbent loaded with 50 wt % PEI, the physical appearance is that of an aggregated paste as opposed to the powder texture that exists prior to PEI loading. This indicates inefficient loading of PEI into the pores and the presence of excess PEI on the particle surface. However, the M30H composite retains its powder form after loading with 50 wt % PEI, which we attribute to the enhanced penetration of PEI deep into the interior pores of the MCM-41 pellet through the pathway provided by the nano-straws. It is also clearly possible for the PEI to fill the lumens of the HNT, but we consider this an additional advantage of the finding that it is possible to design particles that are able to take up an increased level of PEI. The TGA data in Figure 7b show that there are very similar levels of PEI in both MCM-41 and M30H sorbents. We note, however, that as we increase the loading to 60 wt % PEI, the M30H texture also becomes that of a pesty lump showing saturation in loading capacity. This visual observation is an initial indication that the introduction of nano-straws enables more PEI to be loaded onto the composite particles in comparison to MCM-41 alone.

Figure 8a illustrates the CO₂ adsorption and desorption isotherms for 50% PEI-MCM-41 and 50% PEI-M30H sorbents adsorbing pure dry CO₂ gas (90 mL/min) at 75 °C for 2 h and desorbing at 105 °C for 1 h under the flow of N₂ gas. The results show that the M30H sorbent has a superior CO₂ uptake capacity of about 71.3 mg/\(g_{\text{adsorbent}}\) (7.1 wt %) compared to the MCM-41 sorbent having an adsorption capacity of 39.1 mg/\(g_{\text{adsorbent}}\) (3.9 wt %). An initial inspection of the isotherm slopes shows that the 50% PEI-MCM-41 sorbent has a slower adsorption and desorption rate in comparison with the M30H sorbent. An analysis of the initial CO₂ adsorption rates for both sorbents (50% PEI-MCM-41 and 50% PEI-M30H) shown in Figure 8b indicates that the M30H sorbent captures over 60% of its total capacity adsorption capacity (4.6 wt %) within the first 60 s of introducing CO₂ gas. In contrast, the MCM-41 captures just below 30% (1.1 wt %). The adsorption isotherm was fitted to a pseudo-first-order Lagergren adsorption model:

\[
q_t = q_e (1 - e^{-kt})
\]

where \(q_e\) is the equilibrium adsorption capacity and \(q_t\) is the instantaneous adsorption capacity at time \(t\). The adsorption rate constant of \(k = 0.11 \text{ s}^{-1}\) obtained for the 50% PEI-M30H sorbent is 2.2 times greater than the corresponding value for the 50% PEI-MCM-41 sorbent \(k = 0.05 \text{ s}^{-1}\). This shows evidence of a much slower amine encounter rate in the 50% PEI-MCM-41 sorbent when compared to the 50% PEI-M30H sorbent. Again, we posit that this is due to the presence of surface PEI on the MCM-41 sorbent, which provides restrictions to transport into the porous MCM-41, as shown in the schematic of Figure 1. This is understandable considering that the branched PEI having a maximum longitudinal length of 2.1 nm and transverse length of 1.4 nm (structure shown in Figure S1) will have difficulty fully accessing the 3 nm pores of the MCM-41. The phenomenon was also observed by Wang and co-workers with a saturation limit for CO₂ adsorption on hybrid mesoporous MCM-41 impregnated with polymeric amines. The presence of HNTs in the M30H composite thus provides large entry channels to allow access of PEI to the particle interior at multiple entry points directly in the interior and thus create an even distribution of PEI throughout the mesoporous particle. Fitting the adsorption data to a Weber–Morris diffusion model, as shown in Figure S3, further shows that the intraparticle diffusion rate is much higher in the 50% PEI-M30H sorbent (10.4 mg g⁻¹ min⁻⁰.⁵) compared to the 50% PEI-MCM-41 adsorbent (5.5 mg g⁻¹ min⁻⁰.⁵). We also do not discount the fact that the nanotubes provide further sequestration of PEI. The lack of a physical surface layer of PEI also enhances the diffusion rate of CO₂ into the particle. The calculated PEI efficiency (Figure 8c) for 50% PEI-M30H sorbent is 142.6 mg/\(g_{\text{PEI}}\) (3.24 mmol/gPEI) and is 1.8 times

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**Figure 6.** Cut-section TEM images of (a) MCM-41 and (b) MCM-41/HNT composite (M30H). The high-resolution image in b(ii) shows an orthogonal cross-section of HNTs in the composite particle for displaying the lumen of the HNTs.

**Figure 7a** shows photographic images of MCM-41 and M30H adsorbents each loaded with 50 wt % PEI. For the MCM-41 sorbent loaded with 50 wt % PEI, the physical appearance is that of an aggregated paste as opposed to the powder texture that exists prior to PEI loading. This indicates inefficient loading of PEI into the pores and the presence of excess PEI on the surface of the particle. However, the M30H composite retains its powder form after loading with 50 wt % PEI, which we attribute to the enhanced penetration of PEI deep into the interior pores of the MCM-41 pellet through the pathway provided by the nano-straws. It is also clearly possible for the PEI to fill the lumens of the HNT, but we consider this...
that of the spherical 50% PEI-MCM-41 sorbent, which is 78.2 mg/gPEI (1.78 mmol/gPEI). Pure PEI exhibits an even lower efficiency of 45 mg/gPEI (1.45 mmol/gPEI).

**Figure 7.** (a) Photographed images of MCM-41 and M30H sorbents before and after loading with 50 wt % PEI showing that the MCM-41 sorbent become pasty clumps upon loading. (b) TGA weight loss analysis of 50% PEI-M30H and 50% PEI-MCM-41 shows similar levels of PEI in both sorbents.

![Image](https://pubs.acs.org/doi/10.1021/acs.iecr.1c03645/fig/ll/4)

**Figure 8.** (a) CO$_2$ adsorption and desorption kinetics for 50% PEI-MCM-41 and 50% PEI-M30H. (b) Initial adsorption kinetics within the first 1 min of introducing CO$_2$ gas showed that the M30H sorbent has a faster adsorption rate with about 60% of adsorption compared to the MCM-41 sorbents. (c) CO$_2$ adsorption efficiency based on the PEI concentration in the sorbent showed that the M30H composite adsorbent has superior amine efficiency for the CO$_2$ adsorption.

that of the spherical 50% PEI-MCM-41 sorbent, which is 78.2 mg/gPEI (1.78 mmol/gPEI). Pure PEI exhibits an even lower efficiency of 45 mg/gPEI (1.45 mmol/gPEI).

**Figure 9a** shows the CO$_2$ adsorption capacity for the systematic addition of PEI from 10 to 50 wt % PEI into both MCM-41 and M30H. We observe that both adsorbents have similar CO$_2$ uptake capacities at low PEI loading (10 to 30 wt %), and the adsorption capacities increase with the PEI loading. At 40 wt % PEI, the adsorption efficiency for the MCM-41 sorbent begins to decrease from 51 mg/g (5.1 wt %)
to 42 mg/g (4.2 wt %) of CO$_2$ adsorbed. A further small decrease in the CO$_2$ adsorption capacity to 39 mg/g (3.9 wt %) is seen at 50 wt % PEI loading. These observations place the optimum PEI loading for these MCM-41 microspheres at 30 wt % PEI loading with a CO$_2$ adsorption capacity of 51 mg/g$_{\text{adsorbent}}$ (5.1 wt %). For M30H adsorbents, we continue to see an increase in the CO$_2$ adsorption capacity for the M30H sorbent with the increase in PEI loading from 10 to 50 wt %, with the highest CO$_2$ adsorption capacity of 71.3 mg/g$_{\text{adsorbent}}$ (7.1 wt %) observed at 50 wt % PEI. We note that the adsorption capacity for the M30H adsorbent decreases at 60 wt % PEI loading to 39.3 mg/g$_{\text{adsorbent}}$ (3.9 wt %), placing the optimum PEI loading capacity for the M30H sorbent at 50 wt % PEI. The CO$_2$ adsorption capacity of this M30H sorbent at 50 wt % PEI loading (7.1 wt %) shows significant improvements in comparison to previous study on CO$_2$ adsorption onto PEI-impregnated MCM-41 by Le and co-workers, where the measured CO$_2$ adsorption capacity at 50 wt % PEI loading was 2.5 wt %. Figure 9b shows the stability data for PEI-loaded M30H and MCM-41 sorbents over four CO$_2$ adsorption and desorption cycles. The M30H sorbent appears to exhibit a slightly better stability, losing only 0.9% of its initial adsorption capacity over 4 cycles compared to the MCM-41 sorbent that shows a 4.7% decline in adsorption efficiency after 4 cycles.

## CONCLUSIONS

This study describes a method to enhance CO$_2$ capture using PEI sequestered in the high surface area ordered mesoporous structure of MCM-41. The loading of PEI into the pores of the solid adsorbent is hampered by the fact that molecular dimensions are comparable to the pore size of the adsorbent with diffusional barriers inhibiting access to the particle interior. To increase the loading of PEI, we have advanced the concept of introducing HNTs with lumen diameters 15–30 nm into the mesoporous matrix through a one-step facile aerosol-assisted method. The aerosol-assisted method is a ship-in-a-bottle approach to the direct synthesis of MCM-41 in aerosol droplets containing HNTs. The result of such synthesis is a composite particle with a hierarchical pore structure where the larger HNT pores allow entry to the interior of the MCM-41 particle. The concept of interior access is validated by loading PEI onto the composite to yield a solid adsorbent capable of capturing CO$_2$ through chemisorption. The nanostraw composite (M30H) particles allow an enhanced loading of PEI, which we postulate is due to ingress of PEI through the HNT lumen into the interior of the particle. CO$_2$ capture studies indicate a doubling of adsorption capacity upon integration of HNT into MCM-41 (M30H) and loading PEI into these particles. Additionally, the PEI-loaded M30H exhibits a doubling of the capture rate when compared to the system without HNT integration. Continuing work seeks to extend the integration of HNTs to other mesoporous materials such as SBA-15 with larger pore dimensions that can further include functionalized dendritic polyamines.$^{13}$ Small-angle neutron scattering will also be carried out to probe the conformation of PEI or other polymeric amines within the HNT and MCM-41 pores.$^{32,43}$ Such studies will use contrast matching with H$_2$O/D$_2$O mixtures as shown by Bharti and co-workers$^{15}$ to match the scattering length density of silica and will thus highlight PEI assembly in the pores.

The concept of mitigating diffusion limitations in a high surface area mesoporous material such as MCM-41 through the integration of HNTs can be extended to other applications of technological consequence. These include the development of new catalytic systems containing catalytic species in the mesoporous material$^{14}$ and environmental applications of rapid and enhanced contaminant removal. The platform technology that is introduced thus has significant implications to molecular transport in porous media, and the attendant applications are the focus of continued study.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c03645.

2-D and 3-D structures of branched PEI obtained using ChemDraw showing the end-to-end length of the PEI molecule, electron microscopy imaging (SEM and TEM) of Pristine CLA HNTs showing the morphology and dimensions of the nanotubes used in the preparation of the MCM-41/HNT composite, and intra-particle diffusion analysis of CO$_2$ capture data for the 50% PEI-
M30H and 50% PEI-MCM-41 adsorbents based on the Weber–Morris model (PDF)

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Dutcher, B.; Fan, M.; Russell, A. G. Amine-based CO2 capture technology development from the beginning of 2013-a review. ACS Appl. Mater. Interfaces 2015, 7, 2137–2148.
(2) Hahn, M. W.; Steib, M.; Jentys, A.; Lercher, J. A. Mechanism and Kinetics of CO2 Adsorption on Surface Bonded Amines. J. Phys. Chem. C 2015, 119, 4126–4135.
(3) Qi, G.; Wang, Y.; Estevez, L.; Duan, X.; Anako, N.; Park, A.-H.; Li, W.; Jones, C. W.; Giannelis, E. P. High efficiency nanocomposite sorbents for CO2 capture based on amine-functionalized mesoporous capsules. Energy Environ. Sci. 2011, 4, 444–452.
(4) Zhao, A.; Samanta, A.; Sarkar, P.; Gupta, R. Carbon Dioxide Adsorption on Amine-Impregnated Mesoporous SBA-15 Sorbents: Experimental and Kinetics Study. Ind. Eng. Chem. Res. 2013, 52, 6480–6491.
(5) Chatti, R.; Bansiwal, A. K.; Thote, J. A.; Kumar, V.; Jadhav, P.; Lokhande, S. K.; Binwale, R. B.; Labhsetwar, N. K.; Rayalu, S. S. Amine loaded zeolites for carbon dioxide capture: Amine loading and adsorption studies. Microporous Mesoporous Mater. 2009, 121, 84–89.
(6) Gholidoust, A.; Atkinson, J. D.; Hashisho, Z. Enhancing CO2 Adsorption via Amine-Impregnated Activated Carbon from Oil Sands Coke. Energy Fuels 2017, 31, 1756–1763.
(7) Sujan, A. R.; Pang, S. H.; Zhu, G.; Jones, C. W.; Lively, R. P. Direct CO2 Capture from Air using Poly(ethyleneimine)-Loaded Polymer/Silica Fiber Sorbents. ACS Sustainable Chem. Eng. 2019, 7, 5264–5273.
(8) Jana, S.; Das, S.; Ghosh, C.; Maity, A.; Pradhan, M. Halloysite nanotubes capturing isotope selective atmospheric CO2. Sci. Rep. 2015, 5, 8711.
(9) Cai, H.; Bao, F.; Gao, J.; Chen, T.; Wang, S.; Ma, R. Preparation and characterization of novel carbon dioxide adsorbents based on polyethyleneimine-modified Halloysite nanotubes. Environ. Technol. 2015, 36, 1273–1280.
(10) Niu, M.; Yang, H.; Zhang, X.; Wang, Y.; Tang, A. Amine-Impregnated Mesoporous Silica Nanotube as an Emerging Nano-composite for CO2 Capture. ACS Appl. Mater. Interfaces 2016, 8, 17312–17320.
(11) Gaikwad, S.; Kim, Y.; Gaikwad, R.; Han, S. Enhanced CO2 capture capacity of amine-functionalized MOF-177 metal organic framework. J. Environ. Chem. Eng. 2021, 9, 105523.
(12) Liu, Z.-J.; Teng, Y.; Zhang, K.; Cao, Y.; Pan, W.-P. CO2 adsorption properties and thermal stability of different amine-impregnated MCM-41 materials. J. Fuel Chem. Technol. 2013, 41, 469–475.
(13) Lou, Y.; Shantz, D. F. Not all nitrogen atoms are equal: contribution of peripheral versus central amines to the observed reactivity and capture properties of melamine dendrons on SBA-15. Chem. Commun. 2018, 54, 567–570.
(14) Yu, L.; Farinmade, A.; Ajumobi, O.; Su, Y.; John, V. T.; Valla, J. A. MCM-41/ZSM-5 composite particles for the catalytic fast pyrolysis of biomass. Appl. Catal., A 2020, 602, 117727.
(15) Coasne, B.; Hung, F. R.; Pelleng, R. J.-M.; Siperstein, F. R.; Gubbins, K. E. Adsorption of simple gases in MCM-41 materials: the role of surface roughness. Langmuir 2006, 22, 194–202.
(16) Vallet-Regi, M.; Ramila, A.; del Real, R. P.; Pérez-Pareja, J. A New Property of MCM-41: Drug Delivery System. Chem. Mater. 2000, 13, 308–311.
(17) Chen, X.; Lam, K. F.; Yeung, K. L. Selective removal of chromium from different aqueous systems using magnetic MCM-41 nanosorbents. Chem. Eng. J. 2011, 172, 728–734.
(18) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. T.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. A new family of mesoporous molecular sieves prepared with liquid crystal templates. J. Am. Chem. Soc. 1992, 114, 10834–10843.
(19) Kruk, M.; Jaroniec, M.; Kim, J. M.; Ryoo, R. Characterization of Highly Ordered MCM-41 Silicas Using X-ray Diffraction and Nitrogen Adsorption. Langmuir 1999, 15, 5279–5284.
(20) Thi Le, M. U.; Lee, S.-Y.; Park, S.-J. Preparation and characterization of PEI-loaded MCM-41 for CO2 capture. Int. J. Hydrogen Energy 2014, 39, 12340–12346.
(21) Xu, X.; Song, C.; Andreesen, J. M.; Miller, B. G.; Scaroni, A. W. Novel Polyethyleneimine-Modified Mesoporous Molecular Sieve of MCM-41 Type as High-Capacity Adsorbent for CO2 Capture. Energy Fuels 2002, 16, 1463–1469.
(22) Mukherjee, S.; Akshay; Samanta, A. N. Amine-impregnated MCM-41 in post-combustion CO2 capture: synthesis and characterization. Adv. Powder Technol. 2019, 30, 3231–3240.
(23) Loganathan, S.; Tikmani, M.; Ghoshal, A. K. Novel pore-expanded MCM-41 for CO2 capture: synthesis and characterization. Langmuir 2013, 29, 3491–3499.
(24) Lu, Y.; Fan, H.; Stump, A.; Ward, T. L.; Rieker, T.; Brinker, C. J. Aerosol-assisted self-assembly of mesostructured spherical nanoparticles. Nature 1999, 398, 223–226.
(25) Yuan, P.; Tan, D.; Annabi-Bergaya, F. Properties and applications of halloysite nanotubes: recent research advances and future prospects. Appl. Clay Sci. 2015, 112, 75–93.
(26) Abdullayev, E.; Price, R.; Shchukin, D.; Lvov, Y. Halloysite tubes as nanocontainers for anticorrosion coating with benzotriazole. ACS Appl. Mater. Interfaces 2009, 1, 1437−1443.
(27) Owoseni, O.; Nyankson, E.; Zhang, Y.; Adams, S. J.; He, J.; McPherson, G. L.; Bose, A.; Gupta, R. B.; John, V. T. Release of surfactant cargo from interfacially-active halloysite clay nanotubes for oil spill remediation. Langmuir 2014, 30, 13533−13541.
(28) Ojo, O. F.; Farinimade, A.; Trout, J.; Omarova, M.; He, J.; John, V.; Blake, D. A.; Lvov, Y. M.; Zhang, D.; Nguyen, D.; Bose, A. Stoppers and Skins on Clay Nanotubes Help Stabilize Oil-in-Water Emulsions and Modulate the Release of Encapsulated Surfactants. ACS Appl. Nano Mater. 2019, 2, 3490−3500.
(29) Ojo, O. F.; Farinimade, A.; John, V.; Nguyen, D. A Nano composite of Halloysite/Surfactant/Wax to Inhibit Surfactant Adsorption onto Reservoir Rock Surfaces for Improved Oil Recovery. Energy Fuels 2020, 34, 8074−8084.
(30) Keeling, J. L.; Self, P. G.; Raven, M. D. Halloysite in Cenozoic sediments along the Eucla Basin margin. MESA J. 2010, 59, 9−13.
(31) Farinimade, A.; Ojo, O. F.; Trout, J.; He, J.; John, V.; Blake, D. A.; Lvov, Y. M.; Zhang, D.; Nguyen, D.; Bose, A. Targeted and Stimulus-Responsive Delivery of Surfactant to the Oil-Water Interface for Applications in Oil Spill Remediation. ACS Appl. Mater. Interfaces 2020, 12, 1840−1849.
(32) Su, Y.; Wang, Y.; Owoseni, O.; Zhang, Y.; Gamliel, D. P.; Valla, J. A.; McPherson, G. L.; John, V. T. A Bottle-around-a-Ship Method To Generate Hollow Thin-Shelled Particles Containing Encapsulated Iron Species with Application to the Environmental Decontamination of Chlorinated Compounds. ACS Appl. Mater. Interfaces 2018, 10, 13542−13551.
(33) Payne, M. E.; Lou, Y.; Zhang, X.; Sahiner, N.; Sandoval, N. R.; Shantz, D. F.; Grayson, S. M. Comparison of Cross-Linked Branched and Linear Poly(ethylene imine) Microgel Microstructures and Their Impact in Antimicrobial Behavior, Copper Chelation, and Carbon Dioxide Capture. ACS Appl. Polym. Mater. 2020, 2, 826−836.
(34) Ko, Y. G.; Shin, S. S.; Choi, U. S. Primary, secondary, and tertiary amines for CO2 capture: designing for mesoporous CO2 adsorbents. J. Colloid Interface Sci. 2011, 361, 594−602.
(35) Farinimade, A.; Ajumobi, O.; Yu, L.; Su, Y.; He, J.; Valla, J. A.; John, V. A One-Step Facile Encapsulation of Zeolite Microcrystallites in Ordered Mesoporous Microspheres. Ind. Eng. Chem. Res. 2020, 59, 13923−13931.
(36) Kim, S.; Philippot, S.; Fontanay, S.; Duval, R. E.; Lamouroux, E.; Canilho, N.; Pasc, A. pH- and glutathione-responsive release of curcumin from mesoporous silica nanoparticles coated using tannic acid-Fe(III) complex. RSC Adv. 2015, 5, 90550−90558.
(37) Kruk, M.; Jaroniec, M.; Sayari, A. Adsorption Study of Surface and Structural Properties of MCM-41 Materials of Different Pore Sizes. J. Phys. Chem. B 1997, 101, 583−589.
(38) Lvov, Y.; Wang, W.; Zhang, L.; Fakhrrullin, R. Halloysite Clay Nanotubes for Loading and Sustained Release of Functional Compounds. Adv. Mater. 2016, 28, 1227−1250.
(39) Lagergren, S. K. About the theory of so-called adsorption of soluble substances. Sven. Vetenskapsakad. Handingar 1898, 24, 1−39.
(40) Wang, X.; Guo, Q.; Kong, T. Tetraethylenepentamine-modified MCM-41/silica gel with hierarchical mesoporous structure for CO2 capture. Chem. Eng. J. 2015, 273, 472−480.
(41) Weber, W. J.; Morris, J. C. Kinetics of Adsorption on Carbon from Solution. J. Sanit. Eng. Div. 1963, 89, 31−59.
(42) Wu, Y.; Ma, Y.; He, L.; Rother, G.; Shelton, W. A.; Bhatti, B. Directed Pore Uptake and Phase Separation of Surfactant Solutions under Confinement. J. Phys. Chem. C 2019, 123, 9957−9966.
(43) Holewinski, A.; Sakwa-Novak, M. A.; Jones, C. W. Linking CO2 Sorption Performance to Polymer Morphology in Aminopolymer/Silica Composites through Neutron Scattering. J. Am. Chem. Soc. 2015, 137, 11749−11759.
(44) Ajumobi, O.; Su, Y.; Farinimade, A.; Yu, L.; He, J.; Valla, J. A.; John, V. T. Integrating Halloysite Nanostraws in Porous Catalyst Supports to Enhance Molecular Transport. ACS Appl. Nano Mater. 2021, 4, 8455−8464.