

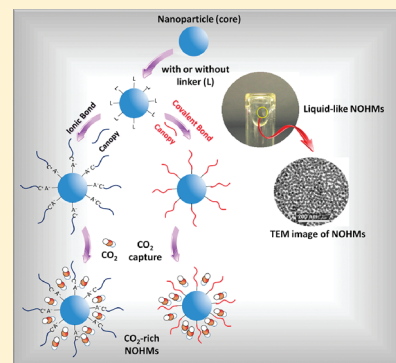
Effects of Bonding Types and Functional Groups on CO₂ Capture using Novel Multiphase Systems of Liquid-like Nanoparticle Organic Hybrid Materials

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S Supporting Information

ABSTRACT: Novel liquid-like nanoparticle organic hybrid materials (NOHMs) which possess unique features including negligible vapor pressure and a high degree of tunability were synthesized and their physical and chemical properties as well as CO₂ capture capacities were investigated. NOHMs can be classified based on the synthesis methods involving different bonding types, the existence of linkers, and the addition of task-specific functional groups including amines for CO₂ capture. As a canopy of polymeric chains was grafted onto the nanoparticle cores, the thermal stability of the resulting NOHMs was improved. In order to isolate the entropy effect during CO₂ capture, NOHMs were first prepared using polymers that do not contain functional groups with strong chemical affinity toward CO₂. However, it was found that even ether groups on the polymeric canopy contributed to CO₂ capture in NOHMs via Lewis acid–base interactions, although this effect was insignificant compared to the effect of task-specific functional groups such as amine. In all cases, a higher partial pressure of CO₂ was more favorable for CO₂ capture, while a higher temperature caused an adverse effect. Multicyclic CO₂ capture tests confirmed superior recyclability of NOHMs and NOHMs also showed a higher selectivity toward CO₂ over N₂O, O₂ and N₂.



INTRODUCTION

Carbon dioxide, CO₂, is one of the greenhouse gases and its atmospheric concentration has increased at an annual rate of about 2 ppm, and thus, the development of efficient CO₂ capture technologies is essential for the future of carbon-based energy. The most commonly employed approach for CO₂ capture is using amine-based solvents that react with gaseous CO₂ to form carbamates.^{1–4} Among the amine-based solvents, monoethanolamine (MEA) is one of the most favored solvents for CO₂ capture due to its high CO₂ capture capacity and fast reaction kinetics. Unfortunately, there are some drawbacks that delay the implementation of MEA in large scale. MEA has high volatility, and therefore, its corrosive fume is a concern for the process design and operation. The concentration of MEA has to be limited to 15–30 wt % and this makes the CO₂ capture and the solvent regeneration processes complicated and costly.^{5,6}

In answer to these concerns associated with MEA, a number of innovative organic and inorganic materials including amine functionalized solid mesoporous sorbents^{7–14} and liquid solvents (i.e., ionic liquids^{15–18} and organic solvents such as aminoalkylsilane^{19,20}) are being developed to capture CO₂. Ionic liquids are particularly intriguing since they generally exhibit negligible vapor pressure even at elevated temperatures. Ionic liquids can be synthesized with task-specific functional groups (e.g., amine groups for CO₂ capture), and they can also possess interesting features such as reversible and phase

changing behaviors.²¹ The current drawbacks of ionic liquids as CO₂ capture media include their complex synthesis and purification steps, and high cost.

Considering these limitations of CO₂ capture solvents, a new class of CO₂ capture medium named nanoparticle organic hybrid materials (NOHMs) has been formulated. Depending on the selection of organic materials, NOHMs can be synthesized in various forms: liquid-like solvent, solid sorbent or gel-like materials. Liquid-like NOHMs are particularly interesting since it can be a direct alternative to MEA solvent. By grafting polymer onto inorganic nanostructures, polymeric chains are anchored to improve the thermal stability, and the resulting NOHMs exhibit near zero vapor pressure at temperatures below their thermal decomposition temperatures. The NOHMs are relatively simple and easy to prepare, and they possess high degree of tunability since both the nanoparticle cores and the polymeric chains can be selected from a wide variety of commercially available materials. Therefore, NOHMs have a great potential for various industrial applications including CO₂ capture.

Earlier versions of the liquid-like hybrid solvents developed at Cornell University were referred to as NIMs (nanoparticle-based

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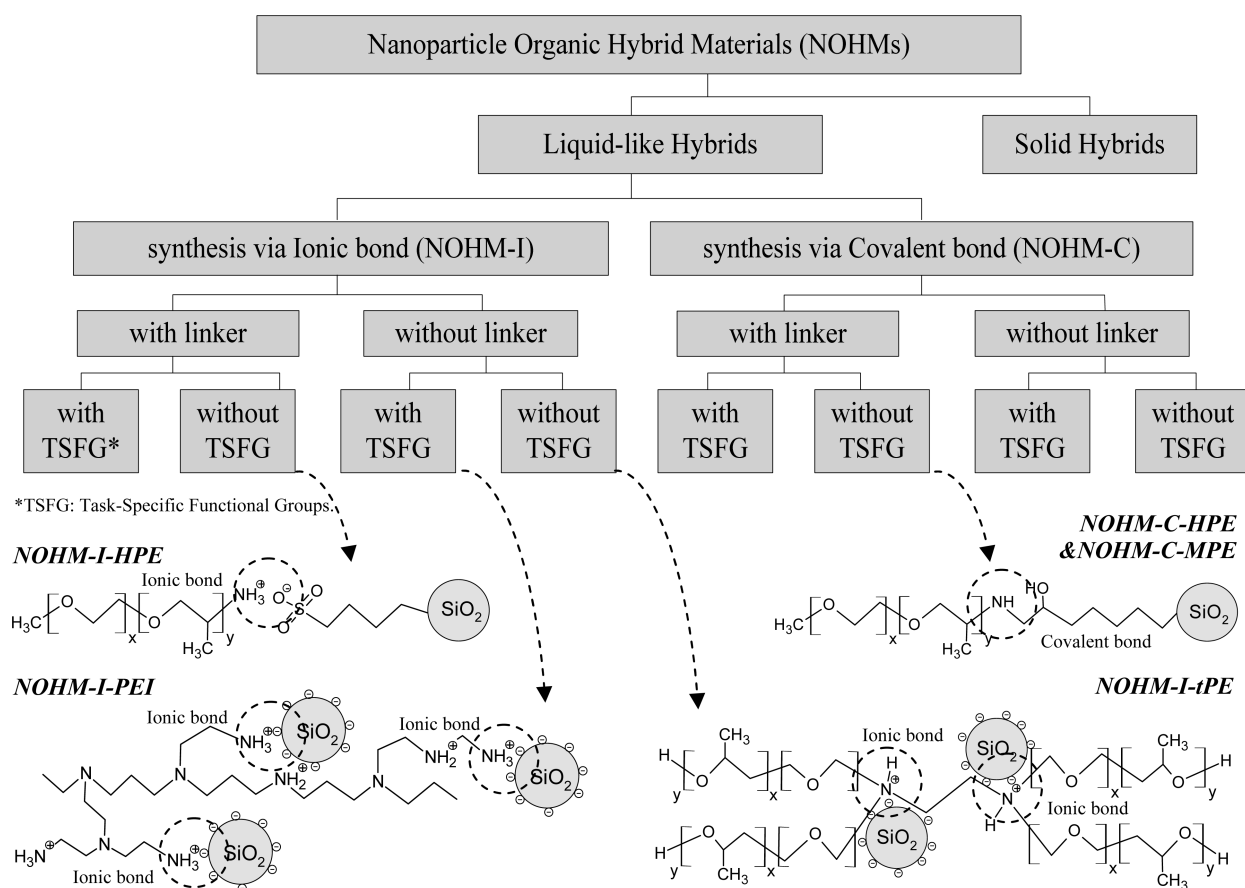


Figure 1. Classification of nanoparticle organic hybrid materials (NOHMs) and the list of five samples: NOHM-I-HPE (linker = sulfonic acid, canopy = polyetheramine); NOHM-I-PEI (no linker, canopy = polyethylenimine); NOHM-I-tPE (no linker, canopy = tertiary amine polyether); NOHM-C-HPE and NOHM-C-MPE (linker = glycidyl ether, canopy = polyetheramine).

ionic materials) and they were synthesized via ionic acid–base reaction between amine and sulfonate groups of polymer chains and nanoparticle cores.^{22–24} In this study, a broader definition of NOHMs was established as a new class of novel materials, and NOHMs were classified based on their representative phase and synthesis methods as well as the existence of task-specific functional groups. Five different NOHMs samples were synthesized using silica nanoparticles (diameter of 10–15 nm) as cores. Both the effects of bonding types (i.e., ionic and covalent bonds) and functional groups (i.e., ether and amine groups) of NOHMs on CO₂ capture were investigated in terms of their thermal stability, CO₂ capture capacity, selectivity, and solvent recyclability.

EXPERIMENTAL SECTION

Chemicals. Silica nanoparticles of 10–15 nm diameter suspended in methanol (MT-ST) and water (Ludox HS-30) were provided by Nissan Chemicals and Sigma Aldrich, respectively. Two different suspensions were used based on the miscibility of selected polymers. For polymeric canopy, two monoamine terminated polyetheramines (ethylene oxide (EO)/propylene oxide (PO) = 31/10 and 6/29, M.W. ~ 2000), tertiary amine (ethylenediamine tetrakis (ethoxylate-block-propoxylate) tetrol, M.W. ~ 7200) and polyethylenimine (M.W. ~ 1800) were obtained from Huntsman, Sigma Aldrich and Polyscience Inc., respectively. (3-glycidyloxypropyl) trimethoxysilane and 3-(trihydroxysilyl)-1-propane sulfonic acid was selected as a linker (also called

corona) and the Dowex HCR-W2 ion-exchange resin was employed during the synthesis of NOHMs.

As shown in Figure 1, NOHMs are first classified based on the representative phase (i.e., liquid-like vs solid hybrids). In this study, only the liquid-like NOHMs were synthesized and evaluated for CO₂ capture. In order to investigate the effects of bonding types and functional groups, five specific NOHMs were prepared: NOHM-I-HPE, NOHM-I-PEI, NOHM-I-tPE, NOHM-C-HPE, NOHM-C-MPE. The nomenclature of NOHMs was designed so that it denotes “NOHM-bonding type-description of polymeric chain including the existence of functional groups.” For example, the second term, “I” and “C”, represents ionic and covalent bonds, respectively. HPE and MPE indicate polyetheramines with “high” (EO/PO = 31/10) and “moderate” (EO/PO = 6/29) amounts of ether groups, whereas “t” denotes “tertiary” amine groups.

Synthesis of NOHMs via Ionic Bond (NOHM-I-HPE, NOHM-I-tPE, and NOHM-I-PEI). Colloidal silica suspension in methanol and 3-(trihydroxysilyl)-1-propane sulfonic acid were diluted with deionized water to prepare 3 wt % silica suspension and 6 wt % silane solution. The silica suspension was added to the silane solution and the pH of this mixture was adjusted to 5 by dropwise adding 1 M NaOH solution. Next, the mixture was slowly reacted at 70 °C for 24 h to ensure complete reaction. In order to remove excess acids, the functionalized silica suspension was then dialyzed (3.5 k MWCO) against deionized water for 48 h. HCR-W2 ion exchange resin was employed to remove Na⁺ ions from the functionalized silica suspension and to protonate the

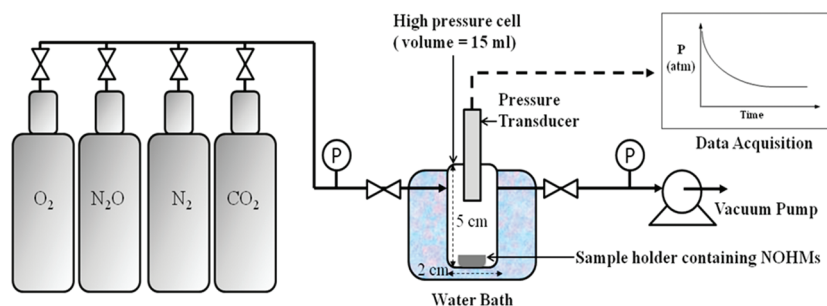


Figure 2. Schematic diagram of experimental setup for CO₂ capture with controlled temperature and pressure.

sulfonate groups. NOHM-I-HPE was synthesized by dropwise adding 10 wt % HPE solution to this functionalized silica suspension.

In case of NOHM-I-*t*PE and NOHM-I-PEI, they were synthesized without linkers, and thus, their preparation steps were slightly different from that of NOHM-I-HPE. Ludox HS-30 was diluted with deionized water to obtain 3 wt % silica suspension. First, Na⁺ of the prepared silica suspension was replaced by protons using HCR-W2 ion exchange resin. While monitoring the reaction pH to reach the equivalent point of 6, NOHM-I-*t*PE was prepared by adding 10 wt % tertiary amine (*t*PE) solution to the functionalized silica suspension. In case of NOHM-I-PEI, due to the large quantity of amine functional groups in the system, the reaction pH did not provide information on the extent of reaction. Therefore, the functionalized silica suspension was mixed with the polymeric solution based on the desired core/canopy ratio. The extent of acid–base reaction as well as the confirmation of ionic bonds was carried out via a thermogravimetric analysis (TGA). The main difference between NOHM-I-*t*PE and NOHM-I-PEI was the existence of the task-specific functional groups in the latter material.

Synthesis of NOHMs via Covalent Bond (NOHM-C-HPE and NOHM-C-MPE). NOHM-Cs were prepared via covalent bond as follows. Three wt% HPE and MPE solutions in ethanol were prepared and a molar equivalence of (3-glycidyloxypropyl) trimethoxysilane was added to each solution. HPE and MPE were selected based on the amount of ether groups in polymeric chains (i.e., high (HPE) and moderate (MPE)). The polyether-silane solutions were then stirred at room temperature for 12 h to ensure complete reaction. The silica suspension prepared in the similar manner as for NOHM-I-HPE was added dropwise into each polyether-silane solution and the resulting mixture was stirred for 5 h and dialyzed (MWCO 3.5k) against deionized water for 48 h to remove excess polyether-silane.

In all cases, to obtain the final NOHMs products, water was removed under vacuum at 35 °C to obtain the final NOHMs. Figure 1(bottom) also illustrates the representative structures of prepared NOHMs.

CO₂ Capture Using NOHMs. The synthesized NOHMs were characterized for physical and chemical properties using a series of analytical tools including transmission electron microscopy (TEM), fourier transfer infrared spectroscopy (Thermo Nicolet 6700 FT-IR Spectrometer with Golden Gate ATR accessory), and TGA (TA Instrument Q50, thermal decomposition at a ramping rate of 5 °C/min under pure oxygen condition). Each FT-IR spectrum from 4000 to 600 cm^{−1} was averaged over 16 scans at 8 cm^{−1} resolution for both pure polymer and NOHMs samples. A high pressure reactor system was constructed with a temperature control (shown in Figure 2) in order to evaluate the

CO₂ capture capacity of NOHMs. The internal volume of the reactor was 15 mL and sample holders were designed so that it can hold about 0.15 g of thin layer of a NOHMs sample to minimize mass transfer problems. The loaded sample holder was placed into the high pressure reactor which was equipped with an online pressure transducer. Before each run, any air or gas in the loaded reactor was removed by applying vacuum ($P_{\text{vacuum}} = 0.0025$ atm). A selected gas (i.e., CO₂, N₂, N₂O, or O₂) was introduced at a desired pressure (1–3.4 atm) and temperature (30–70 °C) and the equilibrium CO₂ capture capacity was then calculated based on the pressure drop using the ideal gas law.

RESULTS AND DISCUSSION

Characterization of NOHMs. Synthesized NOHMs samples were analyzed using the FT-IR to verify the reaction between the primary amines and the surface functional groups of the nanoparticle cores (i.e., ionic bond with sulfonate groups for NOHM-I and covalent bond with glycidyl ether groups for NOHM-C). As shown in Figure 3, the protonated amine peaks confirming the formation of ionic bonding between the polyetheramine and the sulfonate groups were found at 1530 cm^{−1} ($\delta_s(\text{NH}_3^+)$) and at 1630 cm^{−1} ($\delta_a(\text{NH}_3^+)$). The ¹³C NMR result of NOHM-I-HPE in DMSO-*d*₆ (experimental condition: ¹³CO₂ at $P_{\text{CO}_2} = 5$ atm and room temperature) (see Supporting Information (SI) Figure S1) also suggested that CO₂ sorption by NOHMs was mainly due to physisorption rather than chemisorption. In other words, the amine functional groups of the polyetheramines were entirely consumed during the synthesis of NOHMs and the bonds between the nanoparticle core and the grafted polymer chains were very stable. Furthermore, the NOHMs samples did not contain any unreacted free polymers. In case of NOHM-C-HPE, the formation of the polyether-silane was confirmed by the disappearance of a band at 3056 cm^{−1} ($\nu_{\text{C-H}}$ epoxy) and the presence of hydroxyl groups at 3400–3600 cm^{−1} (Figure 3(b)). The similar patterns of FT-IR spectra were found for NOHM-C-MPE and its corresponding polyether-silane.

The physical appearance of the prepared NOHMs under ambient condition was viscous clear or pale yellow liquids as photographed in Figure 4(a). TEM images of NOHMs samples showed that there was no agglomeration observed in NOHMs samples and nanoparticles held self-suspended configurations (Example of TEM images shown in Figure 4(b)). A nanoparticle with surrounding polymeric canopy is defined as one fluid unit of NOHMs

Thermal Stabilities of NOHMs. As polymer chains were tethered onto the surface of nanoparticles, their thermal stability was improved, and this was confirmed from the thermal decomposition

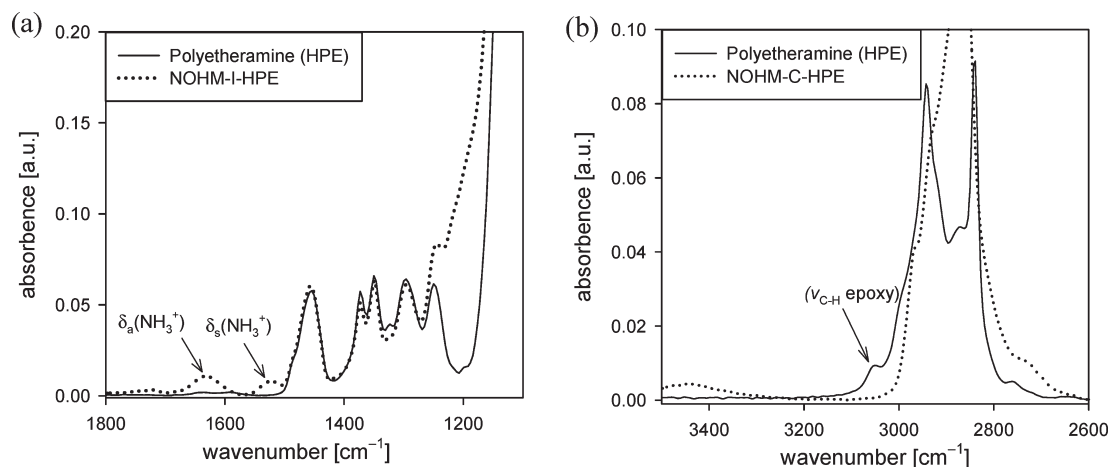


Figure 3. ATR FT-IR spectra of synthesized NOHMs (a) NOHM-I-HPE, (b) NOHM-C-HPE.

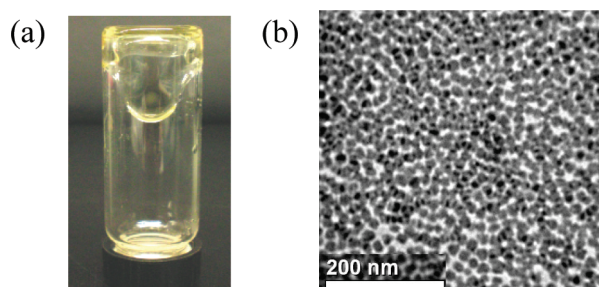


Figure 4. Photo (a) and transmission electron microscopy image (b) of a typical NOHMs sample (NOHM-I-tPE).

experiments performed using a TGA (see SI Figure S2). According to the mass change during the thermal swing, all five NOHMs samples (i.e., NOHM-I-HPE, NOHM-C-HPE, NOHM-C-MPE, NOHM-I-tPE, and NOHM-I-PEI) illustrated 10–40 °C improvement in their thermal stability for given mass changes compared to their corresponding polymers. The improvements in NOHM-C-HPE and NOHM-C-MPE were relatively smaller than those in NOHM-I-HPE. The difference may be due to that 3-(trihydroxysilyl)-1-propane sulfonic acid has higher thermal stability than that of (3-Glycidyloxypropyl)trimethoxysilane. In other words, the coupling agents have significant effects on the thermal stability of synthesized NOHMs. Compared to the thermal decomposition curves of NOHM-I-HPE, NOHM-C-HPE, NOHM-C-MPE, and NOHM-I-tPE, the thermal decomposition curves of polyethylenimine (PEI) and NOHM-I-PEI resulted in faster reduction in mass with the same temperature ramping program because PEI has greater volatility than polyetheramine (HPE and MPE). This implies that the selection of the polymeric chains would also strongly affect the range of the operating conditions of synthesized NOHMs. Similar thermal improvement was observed for NOHM-I-tPE, which was prepared via grafting ethylenediamine tetrakis(ethoxylate-block-propoxylate) onto negatively charged silica nanoparticles. The improvements in thermal stabilities of NOHMs investigated in this study were varied from as low as 10 °C to as high as 40 °C. These are very promising results for CO₂ capture at elevated temperatures of flue gas. Unlike MEA solutions, all NOHMs samples synthesized using polyetheramines showed excellent thermal stabilities with no weight drop until the onset of their

thermal decomposition, indicating negligible vapor pressure over a wide range of operating temperatures. According to the experimental results, the thermal stability of NOHMs can be further optimized by selecting different polymers and linkers.

Effects of Temperature and Pressure on CO₂ Capture Using NOHMs. Since the silica nanoparticles used in this study for the preparation of NOHMs were nonporous, the CO₂ capture in NOHMs was considered to be essentially attributed to the liquid soft materials, the polymeric canopy. Therefore, CO₂ solubilities in NOHMs were expected to follow Henry's law; a linear relationship of CO₂ solubility in NOHMs with respect to the partial pressure of CO₂. A higher CO₂ capture capacity is expected at a higher partial pressure of CO₂. Besides the pressure, temperature also has a significant effect on the CO₂ solubility in NOHMs. Therefore, like other CO₂ capture solvents, NOHMs' CO₂ capture capacity increased with an increase in the partial pressure of CO₂ while the operating temperature showed an adverse effect. The quantity of pure CO₂ stream produced from this separation process would be a function of the slopes of the data shown in Figures 5(a) and (b) and be directly proportional to the differences between initial and final CO₂ pressures and temperatures. For example, according to the data given in Figure 5(a), 0.4 mol of CO₂ can be captured by 1 kg of solvent (canopy portion of NOHM-C-HPE) at $P_{\text{CO}_2} = 3.2$ atm. By exposing this CO₂-rich NOHM-C-HPE to $P_{\text{CO}_2} = 1.3$ atm where NOHM-C-HPE's CO₂ capture capacity is only 0.18 mol-CO₂/kg-solvent, 0.22 mol of CO₂ can be released as the separated product stream. The now CO₂-lean NOHM-C-HPE is then recycled back to the capture reactor for the next separation cycle.

For both pressure and temperature swings, NOHMs synthesized via covalent bond (NOHM-C-HPE) resulted in higher CO₂ capture capacities than those synthesized via ionic bond (NOHM-I-HPE). This was due to the availability of the secondary amine groups in NOHM-C-HPE as previously discussed. If both NOHMs contained the same amount of amine functional groups, the resulting CO₂ capture capacities would have been similar. In both cases of NOHM-I-HPE and NOHM-C-HPE, HPE is an ether-based polymer, and the ether groups in both NOHMs participated in CO₂ absorption owing to its dipole–quadrupole interaction.^{25,26} However, for the operating conditions given in Figures 5(a) and (b) NOHM-C-HPE captured as high as 50% more CO₂ than NOHM-I-HPE while there was only one amine group but 41 ether groups per HPE chain. This

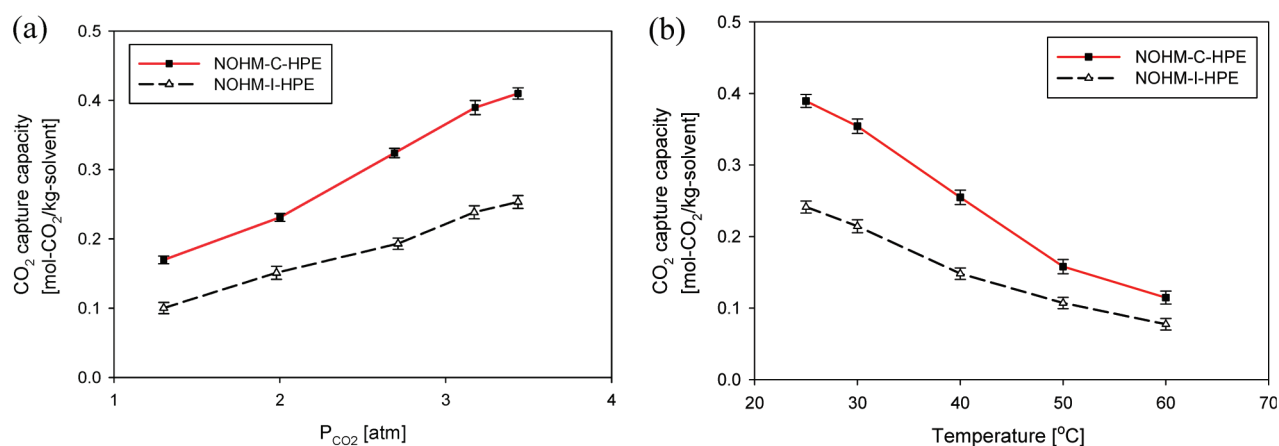


Figure 5. Effect of bonding types used in the synthesis of NOHMs on CO₂ capture capacity as a function of (a) partial pressure of CO₂ at 25 °C and (b) temperature at P_{CO₂} = 3.2 atm.

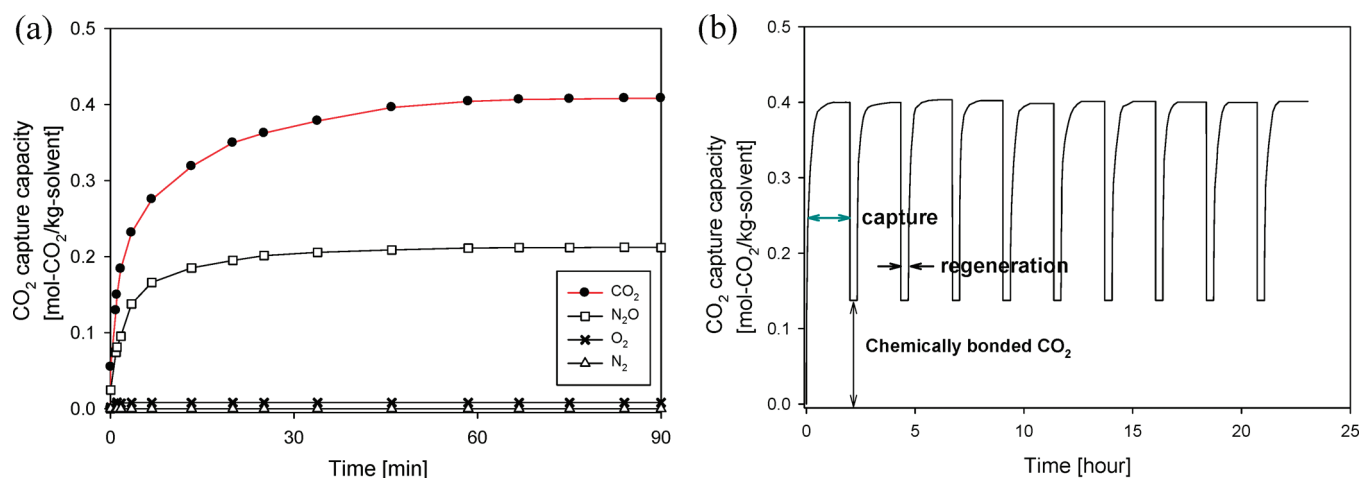


Figure 6. Selectivity and recyclability of NOHMs: (a) Sorption kinetics of CO₂ and other gases in NOHM-C-HPE ($T = 25\text{ }^{\circ}\text{C}$, $P_{\text{CO}_2} = 3.4\text{ atm}$, $P_{\text{N}_2\text{O}} = 3.4\text{ atm}$, $P_{\text{O}_2} = 3.4\text{ atm}$ and $P_{\text{N}_2} = 3.4\text{ atm}$) and (b) Multicycle CO₂ capture using NOHM-C-HPE (Capture conditions: $T = 25\text{ }^{\circ}\text{C}$ and $P_{\text{CO}_2} = 3.4\text{ atm}$; Regeneration conditions: $T = 25\text{ }^{\circ}\text{C}$ and $P_{\text{vacuum}} = 0.0025\text{ atm}$).

implies that the task-specific functional groups such as amine groups are much more effective at CO₂ capture than ether groups. This phenomenon will be further discussed in a later section. Stronger interaction between CO₂ and NOHMs would result in a greater CO₂ capture capacity; however, it could also result in higher energy requirement for solvent regeneration. Thus, a careful optimization of NOHMs system is needed for the economic feasibility of NOHMs' application for CO₂ capture.

Absorption Selectivity of Gases in NOHMs. In addition to the high capture capacity, one of the most important factors required for any capture medium is its selectivity toward the gas of interest, in this case CO₂. With confirmed promising CO₂ capture capacities of NOHMs, a series of subsequent experiments were designed to evaluate the solubilities of other gases in NOHMs samples that exist in flue gas such as nitrogen (N₂) and oxygen (O₂). Nitrous oxide (N₂O) was also evaluated because N₂O is similar to CO₂ in terms of molecular configuration, electronic structure and molecular volume, but different in terms of chemical reactivity with NOHMs' amine groups. In NOHM-I-HPE, CO₂ exhibited the highest solubility among the tested gases, followed by N₂O (see SI Figure S3). Oxygen was found to

be slightly soluble in NOHM-I-HPE, whereas N₂ appeared to be almost insoluble. Since the solubility of gases in liquid phase is governed by the interaction between gaseous and liquid molecules, high solubilities of CO₂ and N₂O in NOHM-I-HPE were expected due to their relatively high quadrupole moments.²⁷ Although the solubilities of CO₂ and N₂O in NOHM-I-HPE were comparable, a significant difference was presented in the solubilities of CO₂ and N₂O in NOHM-C-HPE (Figure 6(a)). This difference could be explained by the existence of the secondary amines in NOHM-C-HPE which can chemically react with CO₂ but not with N₂O. Since NOHM-I-HPE and NOHM-C-HPE both exhibited high selectivity toward CO₂ over N₂, which is the major gaseous component in flue gas, NOHMs have a great potential as a CO₂ capture medium from flue gas or any other gaseous mixtures of CO₂ and inert gases.

Recyclability of NOHMs during CO₂ Capture and Solvent Regeneration Cycles. Another desirable characteristic of CO₂ capture medium is great recyclability because more cycles could be achieved with the solvent; the overall economic feasibility of the separation process would be improved. The regeneration of CO₂-rich NOHMs can be performed either by pressure or

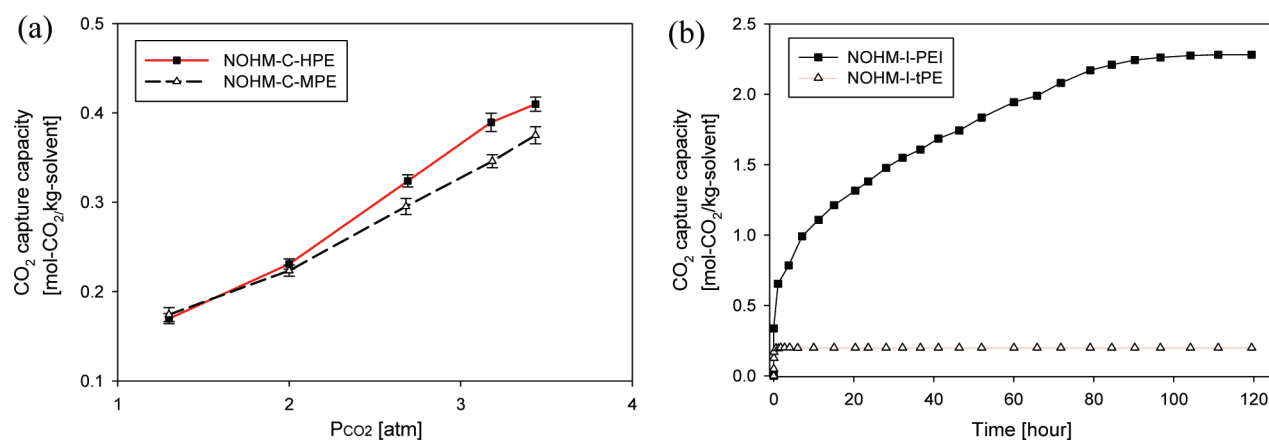


Figure 7. Effect of functional groups on CO₂ capture capacity of NOHMs: (a) Varied ether groups ($T = 25\text{ }^{\circ}\text{C}$) and (b) varied amine groups ($P_{\text{CO}_2} = 3.4\text{ atm}$ and $T = 30\text{ }^{\circ}\text{C}$).

temperature swings. In this study, a pressure swing process was selected to investigate the recyclability of NOHMs during CO₂ capture. First, NOHMs (i.e., NOHM-I-HPE and NOHM-C-HPE) were exposed to CO₂ at 25 °C and $P_{\text{CO}_2} = 3.4\text{ atm}$. Once CO₂ absorption equilibrium was achieved, CO₂-rich NOHMs samples were regenerated under isothermal condition by applying vacuum (0.0025 atm) for 20 min. The regenerated NOHMs samples were then reintroduced to the capture reactor for the next CO₂ capture cycle.

The CO₂ capture capacity of recycled NOHM-I-HPE remained at the same level as that of a fresh NOHM-I-HPE sample even after 10 cycles (see SI Figure S4). Since there were no primary or secondary amines present in NOHM-I-HPE to chemically absorb CO₂, most of interactions between CO₂ and polymeric canopy of NOHM-I-HPE were relatively weak (i.e., physisorption and Lewis acid–base interaction). Therefore, CO₂-rich NOHM-I-HPE was easily regenerated by pressure swing. However, in case of NOHM-C-HPE shown in Figure 6(b), there was a considerable reduction in CO₂ capture capacity after the first cycle. This significant drop was attributed to the chemical bonding of CO₂ and the secondary amine in NOHM-C-HPE which could not be broken by the given pressure swing. Therefore, it was concluded that if the main mechanism of CO₂ capture by NOHMs is chemisorption, the solvent should be regenerated via temperature swing or temperature/pressure swing.

Effects of Ether and Amine Groups on CO₂ Capture Using NOHMs. The effect of functional groups was already briefly discussed in previous sections. Here, two functional groups, ether and amine groups were further investigated to quantify the enhancement of CO₂ capture via chemical interactions. First, NOHM-C-HPE and NOHM-C-MPE were prepared using polyetheramines that have comparable molecular weights but different amounts of ether groups. On average, NOHM-C-HPE contained 41 ether groups, and NOHM-C-MPE consists of 35 ether groups. As shown in Figure 7(a), there was a slight increase in CO₂ solubilities in NOHM-C-HPE compared to that in NOHM-C-MPE. This trend was more significant as the partial pressure CO₂ increased. Interestingly, the ratio between CO₂ capture capacities of NOHM-C-HPE and NOHM-C-MPE at $P_{\text{CO}_2} = 3.4\text{ atm}$ matched the ratio of the amount of ether groups in two NOHMs samples (i.e., 41/35).

In case of amine groups, the effect of functional groups on CO₂ capture was much stronger. In order to investigate this effect, two

NOHMs samples were prepared: NOHM-I-PEI (polyethylenimine-nanoparticle hybrid) and NOHM-I-tPE (synthesized using polyetheramines with tertiary amine groups). At 25 °C and $P_{\text{CO}_2} = 3.2\text{ atm}$, CO₂ capture capacities of starting polymers, tPE and PEI, were about 0.27 mol-CO₂/kg-solvent (equilibrium value) and 2.3 mol-CO₂/kg-solvent (after 80 h, nonequilibrium value), respectively. As shown in Figure 7(b), the existence of amine groups (both primary and secondary amines) significantly increased the CO₂ capture capacity of the NOHMs. Under the same capture conditions (at 30 °C and $P_{\text{CO}_2} = 3.4\text{ atm}$), NOHM-I-tPE exhibited the equilibrium CO₂ capture capacity of 0.2 mol-CO₂/kg-solvent, while NOHM-I-PEI achieved the CO₂ capture capacity of 2.28 mol-CO₂/kg-solvent. This was because as shown in Figure 1 the branched amine groups in NOHM-I-PEI were more readily available to interact with CO₂. The CO₂ capture capacity of NOHM-I-tPE was slightly less than that of tPE and this was because a portion of amine groups was consumed during the synthesis of NOHM-I-tPE.

As illustrated in this study, NOHMs exhibit improved thermal stabilities and therefore, offer a broader range of operating temperatures for CO₂ capture and solvent regeneration. NOHMs in NOHM-I group exhibit lower CO₂ capture capacity than NOHMs in NOHM-C group because the amine groups of the polymers in NOHM-I group were protonated whereas secondary amines in NOHM-C group were available for the reaction with CO₂. It was also found that ether groups on polymer chains of NOHMs enhanced CO₂ capture via Lewis acid–base interactions. The effect of functional groups on CO₂ capture was far more significant when amines were incorporated in NOHMs. NOHMs also exhibit promising recyclability and have a high selectivity toward CO₂ compared to N₂, O₂, and N₂O. With these unique features, NOHMs have shown a great potential for CO₂ capture. As discussed earlier, this particular study was designed to evaluate NOHMs with limited CO₂ targeting functional groups, and therefore, the measured CO₂ capture capacities of NOHMs were less than that of 15–30 wt % MEA solvents. The next generation of NOHMs is currently being synthesized to optimize the CO₂ capture capacity and the mechanistic and kinetic studies are also ongoing. Further investigation for comprehensive understanding of CO₂ capture by NOHMs would not only provide important key factors for the application of NOHMs in CO₂ capture but also offer chemical and physical insights to these novel nanoscale materials.

■ ASSOCIATED CONTENT

S Supporting Information. Figures of ^{13}C NMR of CO_2 pressurized NOHM-I-HPE, thermal stabilities of NOHMs and their corresponding polymers, selectivity and recyclability of NOHM-I-HPE. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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