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Poly(amido amine) dendrimer-incorporated organoclays as efficient adsorbents for capture of NH_3 and CO_2

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HIGHLIGHTS

- The adsorption behavior of gases on dendrimer-loaded organoclays is reported.
- NH_3 gas is preferably adsorbed on carboxyl-terminal of dendrimer in organoclay.
- Similarly CO_2 gas is adsorbed on amine-terminal moiety of dendrimer in organoclay.
- Formation of carbamate species in the latter case is confirmed by solid-state NMR.
- Dendrimer-loaded organoclay is a favorable adsorbent for selective capture of gas.

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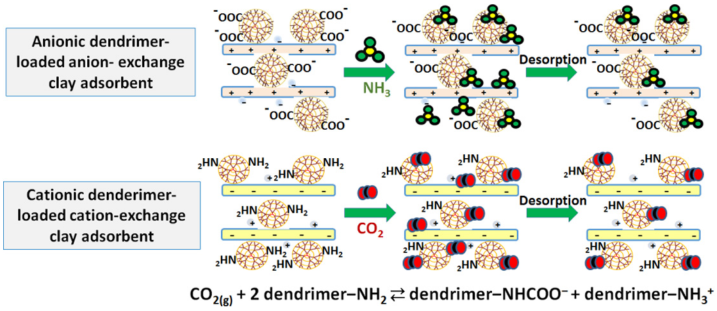
GRAPHICAL ABSTRACT



ABSTRACT

The adsorption performance of gases on poly(amido amine) dendrimer-loaded organoclays has been investigated. In particular, the capture of NH_3 gas on anion-exchange (hydrotalcite) organoclays were assessed and compared to that of CO_2 gas on cation-exchange (sericite and laponite) organoclays, Differently from the adsorption of NH_3 on pristine hydrotalcite, from which NH_3 gases were completely released, the retention of NH_3 on hydrotalcite organoclays was observed. The increase in adsorption capacity for NH_3 with increasing the loading of dendrimer indicated the preferable adsorption of NH_3 on carboxyl-terminated dendrimer moieties and was accompanied by decreases in surface area and pore volume of the organoclays. Similar behaviors were referred for the selective adsorption of CO_2 on amine-terminated dendrimer moieties of laponite and sericite organoclays. Measurements by solid-state ^{13}C NMR of adsorbed isotope-enriched $^{13}CO_2$ confirmed the formation of carbamate species. These results show that dendrimer-loaded organoclays are favorable solid adsorbents for the efficient and recognized capture of gases such as NH_3 and CO_2.

1. Introduction

Air pollution and climate change are major issues in relation to the global warming and greenhouse effect. Accordingly, the scientific community is working to reduce the emission of greenhouse gases and volatile toxic compounds through the development of

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new technologies, for instance, the design of effective adsorbents to be solved environmental issues [1–4]. Ammoniates are known to be the second most widely produced industrial chemicals [5] and the atmospheric content of ammonia exceeding 100 ppm may be hazardous to human, causing respiratory and allergic diseases [6,7]. Thus, considerable R&D efforts have been made in controlling the NH_3 emission. Relevant technologies include combustion, gas reaction, catalytic conversion, capture by adsorption/absorption and so on [8–10]. For the latter, porous materials with tailorable surface properties such as zeolites [11], activated carbons [9,12–14], metal/organic frameworks [15], and clays [16] have been used as gas adsorbents due to their large surface areas, adjustable pore sizes, controllable properties, and high thermal stabilities. Among various solid adsorbents, activated carbons are commonly utilized for NH_3 capture [13,17,18]. However, they require calcination treatment at elevated temperatures to attain desirable porosity [13,14] and, in many cases, protonation of NH_3 during the adsorption process [12,13] and simultaneous desorption [14] are inevitable. In this context, organoclays are recognized as the alternative materials for gas adsorption owing to the presence of multiple active sites available for the adsorption of inorganic as well as organic molecules [4,19,20].

Poly(amido amine) (PAMAM) dendrimers are organic molecules with highly branched three dimensional spherical morphology and abundant terminal functional groups. Nonetheless, while carbon-based adsorbents have been used for NH_3 gas adsorption [21], few reports in the scientific literature on clay adsorbents are available [22,23]. We report herein the capture of NH_3 on cation- and anion-exchange clays and organoclays decorated with amine- and carboxylate-terminated PAMAM dendrimers, respectively. The NH_3 adsorption performances were studied on pristine clays and organoclays with different properties such as surface area, pore volume, and pore size. The results obtained were compared with that of CO_2 adsorption, which have been examined previously under similar experimental conditions [4]. In addition, the interaction of gas adsorbate with dendrimer moieties were investigated by means of solid-state NMR spectroscopy.

2. Experimental section

2.1. Materials

Laponite (type XLG) and hydrotalcite clays were obtained from Southern Clay Products Inc., USA, and Wako Chemicals, Japan, respectively. Sericite clay (type FSN) was donated from Sanshin Mining Ind. Co. Ltd., Japan. Amine-terminated fourth generation (G4.0) and carboxylate-terminated (G4.5) PAMAM dendrimers (MW 14,213 and 26,258, respectively) dissolved in methanol were purchased from Sigma Aldrich, USA. Concentrated HCl and an aqueous ammonium hydroxide (35 wt%) solution were products of Fisher Scientific, USA. All chemicals were used without purification.

2.2. Preparation of organoclays

Organoclays were prepared following an ion-exchange process reported elsewhere [4,19]. In brief, the aqueous dispersion of pristine clay and dendrimer was adjusted to pH 4 and continuously stirred for 2 days at 70 °C. The product was then collected by centrifugation and vacuum-dried for 6 h. Amine-terminated PAMAM dendrimer was used for subsequent hybridization process with laponite and sericite, whereas its carboxylate-terminated counterpart was hybridized with hydrotalcite. Then organoclays prepared are denoted as Lap*n*, Ser*n*, and Hyd*n*, respectively, where *n* represents the weight ratio of dendrimer versus clay.

2.3. Gas adsorption and desorption study

The adsorption of NH_3 was carried out on a gas adsorption system, as described previously [24]. The system is consisted of two major components, namely a gas generation/condensation chamber (G-1 and G-2; volume 1 L) and a gas adsorption chamber hanging a sample holder (A-1; 500 mL). Typically, NH_3 gas evaporated from an aqueous ammonium hydroxide solution (200 mL) at 40 °C in the G-1 chamber was allowed to adsorb on the powdered adsorbent in the A-1 chamber for 300 min. When the excessive NH_3 gas and H_2O vapour were condensed into an aqueous ammonium hydroxide solution (200 mL) in chamber G-2 at room temperature and a solution in G-1 decreased, the G-2 was used as the evaporation chamber and *vice versa*. Temperature dependence on NH_3 gas adsorption was carried out within a temperature range of 40–150 °C. The desorption experiments were performed for adsorbents adsorbed NH_3 gas for 100 min. The NH_3 adsorption and desorption capacities of adsorbents were determined by gravimetric method on a thermogravimetric analyzer (Q500, TA instrument).

2.4. Brunauer–Emmett–Teller (BET) and solid-state NMR measurements

Nitrogen (N_2) adsorption/desorption isotherms were measured at 77 K on a physisorption instrument (BELSORP-max, BEL, Japan). Prior to each measurement, free adsorbents (clays or organoclays) were pre-treated at 120 °C in a vacuum for at least 3 h. Whereas, adsorbents loaded NH_3 or CO_2 adsorbates were directly used for the N_2 adsorption/desorption isotherm measurements without further treatment. NH_3-adsorbed adsorbents were prepared as described above and the preparation of CO_2-adsorbed adsorbents were followed the procedure previously reported [4]. Accordingly the properties, namely, surface area, pore size, and pore volume of adsorbents were derived from the isotherm data by means of conventional methods.

The interaction of CO_2 with dendrimer-incorporated organoclays was studied by solid-state ^{13}C CP-MAS NMR at room temperature. All ^{13}C NMR spectra were recorded on a wide-bore 11.75 Tesla spectrometer (Avance III, Bruker-Biospin) operating at a Larmor frequency of 125.76 MHz. Prior to the NMR measurement, the specimen (clay or organoclay powder, 100 mg) was packed into a 3.2 mm MAS rotor (under N_2 atmosphere), which was placed in a standard glass tube (10 mm o.d.) fitted with stopcocks. The sealed glass tube was then connected to a vacuum manifold, followed by an evacuation treatment (pressure $<10^{-5}$ Torr) at room temperature for 2 h. Subsequently, isotope-enriched $^{13}CO_2$ gas (enrichment level 99%, Cambridge Isotope Lab., Inc.) was introduced into the evacuated sample at room temperature and an equilibrium partial pressure of 500 Torr. After sat for 2 h, the sealed glass tube was then transferred to a glove box and the sample-loaded rotor was capped gas-tight under N_2 atmosphere.

3. Results and discussion

3.1. Adsorption and desorption of NH_3

To improve the adsorption capacity, the clay adsorbents may be hybridized with other adsorbing moieties. We have chosen to immobilize PAMAM dendrimers on clays through an ion-exchange process owing to their numerous terminal functional groups and flexible structure [18,25,26]. Here, sericite and laponite organoclay adsorbents were prepared by immobilizing amine-terminated G4.0 PAMAM dendrimer on cation-exchange sericite and laponite clays, respectively. Whereas, hydrotalcite organoclay adsorbents were fabricated by hybridizing anion-exchange hydrotalcite clay with carboxylate-terminated G4.5 PAMAM dendrimer.

For the measurements of NH_3 adsorption on organoclays, since an aqueous ammonium hydroxide solution was used as the source of NH_3 gas, the co-adsorption of H_2O was inevitable. Thus, the adsorption capacity of NH_3 was derived by subtracting the amount of adsorbed H_2O, although it was negligibly small (less than 0.8 mg/g(adsorbent)) compared to NH_3 at low temperature, as shown in Fig. 1(A). Fig. 1(B) shows the H_2O-subtracted net NH_3 adsorption capacity of various organoclay adsorbents with different mixing ratios (0.0–0.7) of PAMAM dendrimers. Among them, the NH_3 adsorption capacity on organoclays tends to follow the trend of hydrotalcite ≫ sericite > laponite. This clearly indicates that anion-exchange hydrotalcite loaded with anionic dendrimers (*i.e.*, hydrotalcite organoclay) exhibits a remarkably high NH_3 adsorption capacity compared to cation-exchange clays (such as sericite and laponite) loaded with cationic dendrimers (*i.e.*, sericite and laponite organoclays). Moreover, unlike hydrotalcite organoclay adsorbents, by which a significant increase of NH_3 adsorption capacity with increasing dendrimer/clay weight ratio was observed and gradually level off at the mixing ratio of ⩾0.5 g/g(clay) (see Fig. 1(B)), a mild decrease in total NH_3 adsorption with increasing the mixing ratio was observed for both sericite and laponite organoclay adsorbents. These trends observed for NH_3 adsorption on aforementioned organoclays were completely opposite to those observed previously for CO_2 adsorption [4]. Namely, the CO_2 adsorption capacity tended to decrease with increasing the mixing ratio for hydrotalcite organoclays but an opposite trend was observed for both sericite and laponite organoclays with a similar threshold value of mixing ratio (⩾0.5 g/g(clay)) for saturation of adsorption [4].

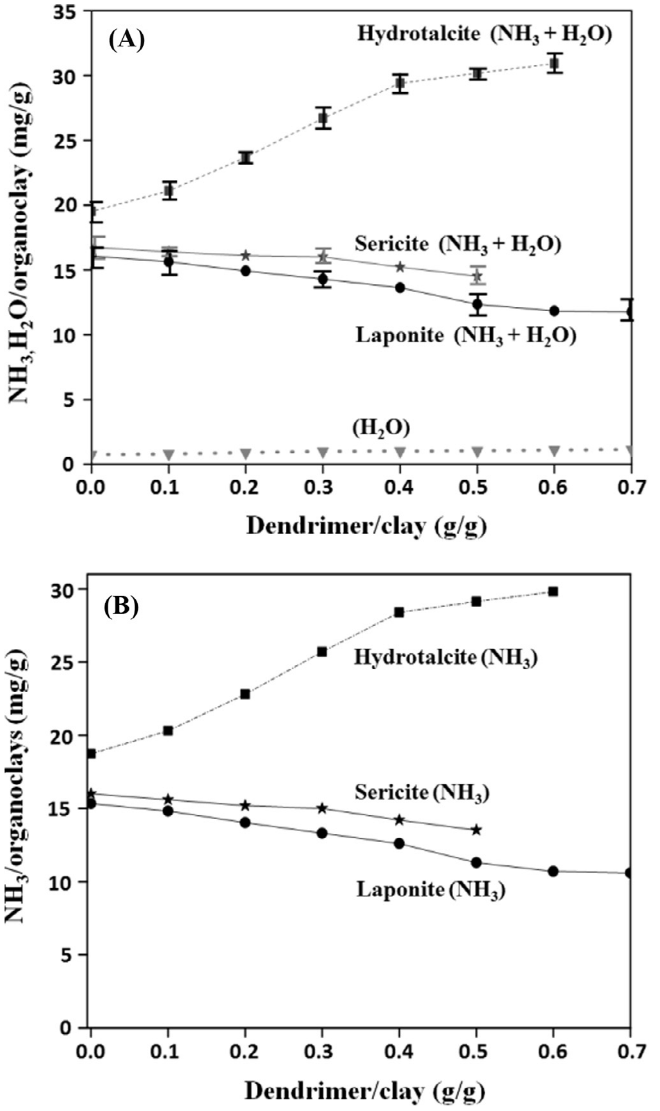


Fig. 1. NH_3 adsorption of organoclay adsorbents with different PAMAM dendrimer mixing ratios measured at 40 °C. (A) NH_3 adsorption including H_2O. (B) Net NH_3 adsorption subtracted H_2O.

To afford more insights of gas adsorption and release on the hydrotalcite organoclays, which exhibited a superior NH_3 adsorption performance (Fig. 1), additional measurements were also performed for NH_3 desorption. The total net amount of desorbed NH_3 was found to decrease gradually with increasing dendrimer content, as shown in Fig. 2 (curve d). Accordingly, the amount of NH_3 remained in the organoclay adsorbents can be derived by subtracting the values observed for desorption (curve d) from those of the adsorption (curve a), leading to a difference profile (curve a–d). The residual NH_3 molecules remaining on the organoclays determined show similar profile with that of the adsorption, *i.e.*, the net amount gradually increased with increasing dendrimer content and approached a plateau value, although nearly null amount of NH_3 was remained on the pristine hydrotalcite (Hyd0.0) clay. These results indicate the strong and preferential adsorption of NH_3 on the dendrimers in organoclays. Similar observation could be referred for CO_2 adsorption on laponite organoclays [4].

Since the evaporation of NH_3 gas depends on the heating temperature of an aqueous ammonium hydroxide solution, the adsorption may change with the heating temperature. Fig. 3 displays the variations of NH_3 adsorption capacity as a function of temperature for the pristine and PAMAM dendrimer-loaded hydrotalcite clays. The pristine hydrotalcite (Hyd0.0) exhibited an overall NH_3 and H_2O (curve a; Fig. 3(A)) adsorption that increased from 18.6 mg/g (adsorbent) at 40 °C to 25.2 mg/g(adsorbent) at 150 °C. Among them, the amount of adsorbed H_2O vapour was very low at temperatures below 70 °C due to low vapour pressure. However, a remarked increase in H_2O adsorption with increasing temperature above 90 °C (curve b; Fig. 3(A)) was observed at a threshold temperature that is just below the boiling point of water. As a result,

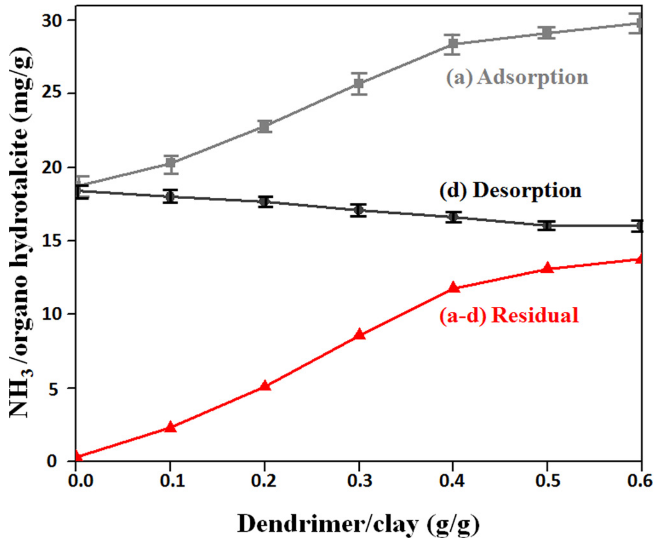


Fig. 2. Adsorption (a) and desorption (d) of net NH_3 on hydrotalcite organoclay adsorbents with different PAMAM dendrimer mixing ratios measured at 40 °C. (a–d) the residual amount of NH_3 remained in the corresponding organoclay adsorbents.

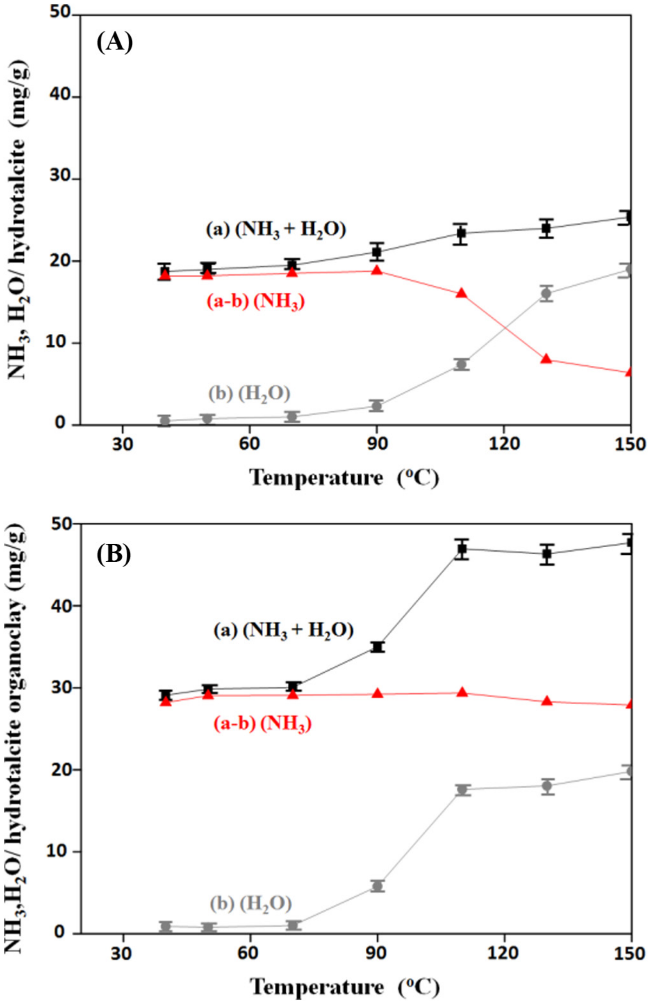


Fig. 3. NH_3 adsorption with temperature observed for (A) pristine hydrotalcite (Hyd0.0) and (B) hydrotalcite organoclay (Hyd0.6) adsorbents. (a) NH_3 adsorption including H_2O, (b) only H_2O, (a–b) Net NH_3 adsorption subtracted H_2O.

the net NH_3 adsorption on the pristine hydrotalcite adsorbent at various temperatures can be determined by simple subtraction, as shown in curve a–b (Fig. 3(A)), which showed a remarkable decrease with temperature above 90 °C. On the other hand, while the hydrotalcite organoclay (Hyd0.6) showed an adsorption curve for the co-adsorption of NH_3 and H_2O similar to that of pristine hydrotalcite at temperature below 70 °C, overall adsorption was rapidly increased at the temperature above 90 °C and eventually reached a plateau value above 110 °C (curve a; Fig. 3(B)). Similar temperature-dependent profile can be referred for the adsorption of H_2O with much lower adsorption values (curve b; Fig. 3(B)). In this case, the net NH_3 adsorption curve with adsorption values of 27.8–28.8 mg/g(adsorbent) was nearly independent of temperature (curve a–b; Fig. 3(B)). This behavior is rather different from the CO_2 adsorption curve observed for the laponite organoclay, which gradually decreases to nearly zero at temperatures above 150 °C [4].

It is noteworthy that, based on the results in our previous report [4], the dependences of CO_2 adsorption capacity on dendrimer content in organoclays were completely opposite to those observed for NH_3 adsorption. In brief, the CO_2 adsorption capacity on laponite and sericite organoclays was increased with increasing dendrimer content, but a reverse trend was observed for hydrotalcite organoclays, although similar to NH_3 adsorption, a threshold dendrimer content of $\geqslant 0.5$ g/g(clay) for saturation adsorption was also observed for CO_2 [4]. This threshold dendrimer content is similar to the tendency of dendrimer content on both cation- and anion-exchange pristine clays [4].

3.2. Comparison of gas adsorption behaviors

The adsorption behaviors of NH_3 and CO_2 on organoclays reported here are rather different and, hence, deserve further investigation. Different organoclay adsorbents exhibit different selectivity toward NH_3 and CO_2 adsorbates. The NH_3 molecule tends to preferentially adsorb on hydrotalcite loaded with carboxylate-terminated dendrimers (see Fig. 1). This result is in contrast to the preferable adsorption of CO_2 on sericite and laponite clays loaded with amine-terminated dendrimer [4]. Clearly, the selective adsorption behaviors may be closely related to the surface properties of the organoclay adsorbents. By comparing with the results obtained from corresponding pristine clays, which showed practically non-selective adsorption of NH_3 and CO_2, it is clear that the nature of the loaded PAMAM dendrimer plays the key role for selective adsorption. To clarify this point, the properties of clay adsorbents before and after loading of functional dendrimers were examined and compared in the presence or absence of respective adsorbate.

The N_2 adsorption/desorption isotherms of clay adsorbents measured before and after NH_3 and CO_2 adsorption are shown in Fig. 4. Accordingly, surface area (S_{BET}), total pore volume (V_{tot}), and average pore size (d_{BJH}) of adsorbents before and after the gas adsorption can be determined, as listed in Table 1. Also listed in Table 1 are the types of isotherm observed for different guest-host adsorption systems identified according to the Brunauer-Deming-Deming-Teller (BDDT) classification proposed by the IUPAC [27]. Among various adsorbents, pristine clays and organoclays of hydrotalcite and sericite showed nonpores type-III isotherms (denoted as III_{non}) both before and after the adsorption of both NH_3 and CO_2 adsorbates. On the other hand, the pristine laponite clay and laponite organoclay adsorbents exhibited the mesoporous Type-IV isotherm with H2 hysteresis loop (denoted as IV-H2) before and after the adsorption of adsorbates, except for the laponite organoclay after adsorption of CO_2 (which showed III_{non}-type isotherm). The observed variations in isotherm types therefore depend on the structural properties of various adsorbents (Fig. 4 and Table 1).

As can be seen from Table 1, while different pristine clays and PAMAM dendrimer-modified organoclays showed different properties before and after adsorption of NH_3 or CO_2, the BET surface areas normally decrease with dendrimer content and in the presence of gas adsorbates, indicating the occupation of surface area by dendrimer incorporation and by selective gas adsorption. However, the amount of change in S_{BET} depends largely on the type of clay or organoclay adsorbent, dendrimer content, and type of gas adsorbate. In general, decreases in S_{BET} of adsorbents happened after the adsorption of NH_3 compared to that of CO_2 adsorbate. Moreover, among various organoclay adsorbents, considerable decreases in S_{BET} were observed for hydrotalcite organoclay after the adsorption of NH_3, whereas significant reductions in S_{BET} were found for sericite and laponite organoclays in the presence of adsorbed CO_2, as shown in Table 1. The above results provide additional supports to the notion that selective adsorption occurs during uptake of NH_3 and CO_2 on different organoclays.

Similar conclusions may also be drawn on the variations of V_{tot} with dendrimer content as well as the presence of NH_3 or CO_2 adsorbate molecules. The V_{tot} was decreased with dendrimer content and in the presence of a gas adsorbate. In particular, remarkable decreases from pristine clay were observed for the hydrotalcite organoclay adsorbents in the presence of adsorbed NH_3. Similar decreases in V_{tot} can be observed for the sericite and

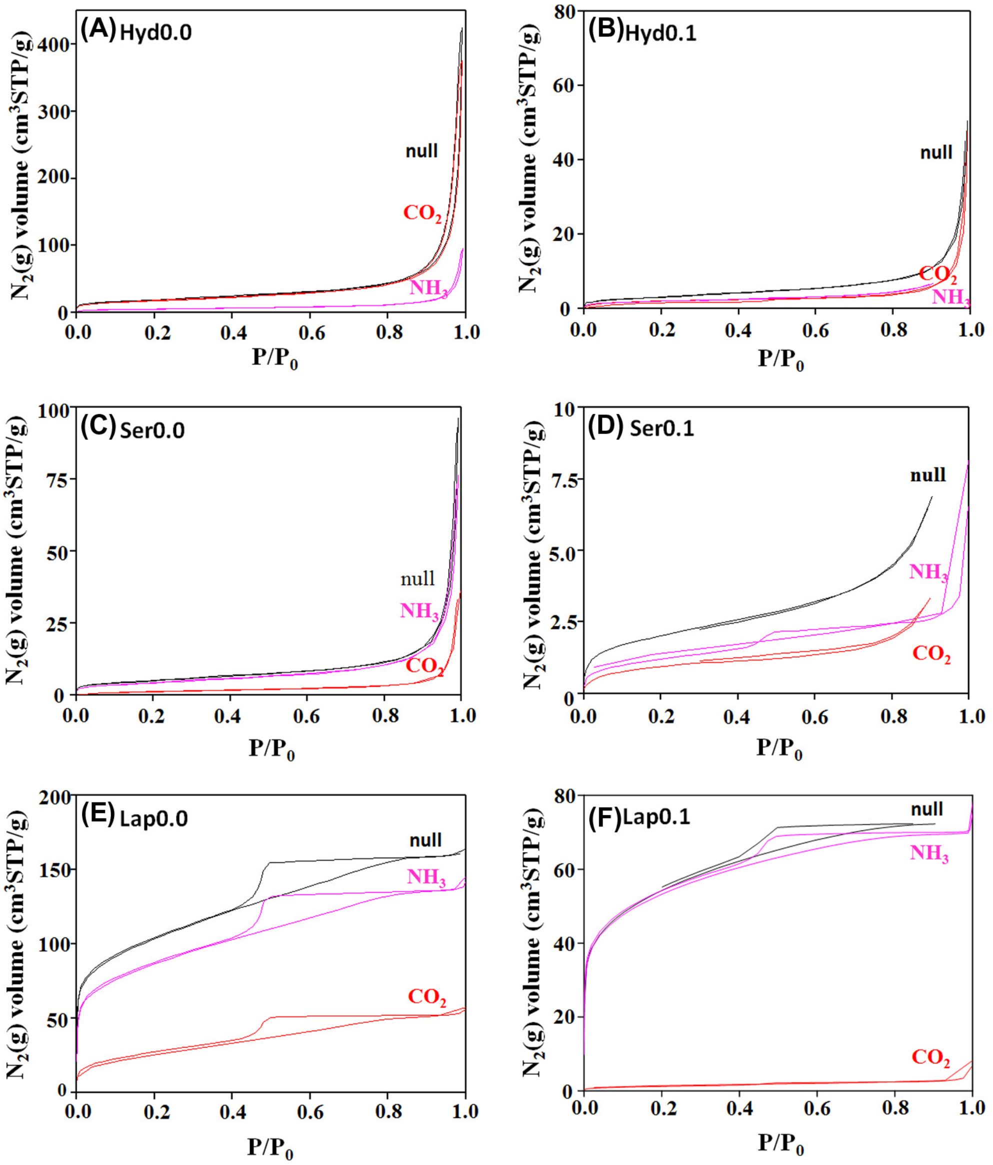


Fig. 4. Nitrogen Isotherm at 77 K for pristine clays (0.0) and organoclays (0.1) before and after NH_3 or CO_2 adsorption.

Table 1
Properties of pristine clay and organoclay adsorbents.

Adsorbent	Isotherm type[a]			S_{BET} (m^2/g)[b]			V_{tot} (cm^3/g)[c]			d_{BJH} (nm)[d]		
	Null	NH_3	CO_2	Null	NH_3	CO_2	Null	NH_3	CO_2	Null	NH_3	CO_2
Hyd0.0	III_{non}	III_{non}	III_{nop}	67.6	13.6	64.2	0.65	0.08	0.58	18.9	19.0	18.0
Hyd0.1	III_{non}	III_{non}	III_{non}	46.2	0.9	43.6	0.58	< 0.01	0.52	19.5	22.6	19.7
Ser0.0	III_{non}	III_{non}	III_{non}	18.1	8.3	15.9	0.13	0.04	0.11	10.5	10.5	10.7
Ser0.1	III_{non}	III_{non}	III_{non}	11.6	5.1	3.3	0.08	0.02	0.01	11.1	12.7	11.1
Lap0.0	IV-H2	IV-H2	IV-H2	361.0	18.1	302.3	0.25	0.07	0.22	2.8	3.3	2.9
Lap0.1	IV-H2	IV-H2	III_{non}	148.9	16.8	7.3	0.11	0.04	0.01	3.4	4.3	3.9

[a] III_{non} = nonpores type-III; IV-H2 = mesoporous type-IV with H2 hysteresis loop.
[b] Brunauer-Emmett-Teller (BET) surface area determined from the adsorption branch of the N_2 adsorption/desorption isotherm (77 K).
[c] Total pore volume.
[d] Pore size distribution calculated with the Barrett-Joyner-Halenda method.

laponite organoclays in the presence of adsorbed CO_2. On the other hand, slight increases in d_{BJH} with dendrimer content were observed. The marginal increase in pore size has been ascribed due to breathing of adsorbent systems [28]. In general, the pore size was independent of the presence of an adsorbate (NH_3 or CO_2) and on the order of hydrotalcite > sericite > laponite differently from surface area and pore volume.

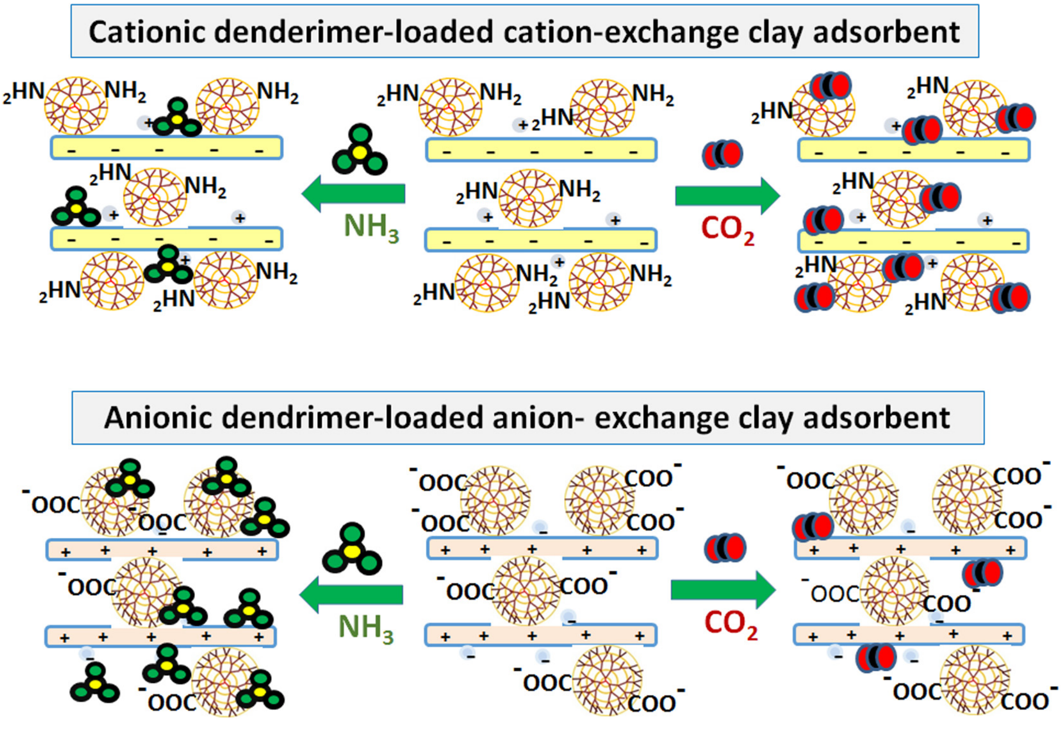
The noticeable decreases in S_{BET} and V_{tot} observed for all adsorbents in the presence of NH_3 may be ascribed to the presence of H_2O during the adsorption process [14]. Nevertheless, the corresponding decrease in S_{BET} and V_{tot} observed for the NH_3-adsorbed hydrotalcite organoclay (Table 1) is much more significant and clearly indicates the efficient adsorption of NH_3 on carboxylate-terminated dendrimers loaded on the hydrotalcite clay. Hence, the carboxylate species on hydrotalcite organoclay should be the active adsorption site of NH_3. On the other hand, more remarkable decreases in S_{BET} and V_{tot} from pristine clay were observed for sericite and laponite organoclays in the presence of CO_2 than NH_3. In this context, the amine species in dendrimers loaded on respective clays should be responsible for the selective adsorption of CO_2 on these organoclay adsorbents. Due to selective and strong adsorptions between NH_3 with carboxylate groups on hydrotalcite organoclays and CO_2 with amine groups on sericite and laponite organoclays, respectively, some residual adsorbates were remained in the adsorbents even after the desorption process (see Fig. 2 and Ref. [4]). In other words, NH_3 adsorbate is more affinitive to carboxylate-terminated dendrimers rather than their amine-terminated counterparts. On the contrary, CO_2 is affinitive to amine-terminated dendrimers rather than carboxylate-terminated dendrimers. These findings are in excellent agreement with previous adsorption kinetics studies of CO_2 on organoclays [29].

The analytical investigation of adsorption kinetics of CO_2 gas on organoclays clarified that the gas adsorption on organoclays was managed by three independent adsorption sites of clay surface, clay interlayer and dendrimer [29]. By Combining with the results obtained in this investigation, the aspect of adsorption of NH_3 gas as well as CO_2 gas on clays can be illustrated in Scheme 1. Although pristine clays do not possess any specific functional moieties for adsorption of NH_3 and CO_2 gases, some gas molecules can still be adsorbed on porous clay surface and within interlayer of clay sheets. However, the situation is different, when dendrimers are loaded in clays: Cation-exchange and anion-exchange clays behave differently, since amine-terminated and carboxylate-terminated dendrimers, respectively, are ion-exchanged. Then the NH_3 gas is selectively absorbed on anionic dendrimer of hydrotalcite organoclays besides on hydrotalcite, and the NH_3 gas adsorbed on dendrimer is not easily desorbed, different from NH_3 gas adsorbed on clay that is easily desorbed. On the other hand, the NH_3 gas is scarcely adsorbed on the amine-terminated dendrimer in cation-exchange organoclays. This indicates that there is no specific binding moiety for NH_3 gas on amine-terminated dendrimer in organoclay. The situation of CO_2 gas adsorption on organoclays is completely inverse to it of NH_3 gas adsorption. CO_2 gas is tightly absorbed on amine-terminated dendrimer in cation-exchange organoclays, but CO_2 gas scarcely adsorbs on carboxylate-terminated dendrimer in anion-exchange organoclays and the CO_2 adsorption happens on clay itself of anion-exchange organoclays [4].

3.3. Identification of dendrimer-gas interaction

To identify guest-host interactions between adsorbate molecules and dendrimer-immobilized organoclay adsorbents, we investigated the solid-state NMR spectroscopy. However, to avoid complications arising from the co-adsorbed H_2O during NH_3 adsorption studies, we have chosen to elucidate this phenomenon by using an alternative adsorption system, namely, the adsorption/desorption of CO_2 on laponite-based adsorbents. Moreover, to ensure adequate signal sensitivity, isotope-enriched $^{13}CO_2$ gas was adopted as the adsorbate. The solid-state ^{13}C NMR spectra obtained for the pristine laponite (Lap0.0) and laponite organoclay (Lap0.1) after adsorption and desorption of $^{13}CO_2$ are shown in Fig. 5. Two resonance signals with ^{13}C chemical shift ($\delta^{13}C$) of 162 and 167 ppm observed for the $^{13}CO_2$-adsorbed pristine laponite can be assigned due to carbon on the bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) groups, respectively (Fig. 5A). Since the pristine laponite clay examined has sodium silicate ($Si–O^-Na^+$) moiety on its surface, it tends to react with the adsorbed CO_2 to form sodium bicarbonate in the presence of H_2O, which can be expressed by Eq. (1):

$$CO_{2(g)} + clay - O^-Na^+ + H_2O \leftrightarrows clay - OH + NaHCO_3 \quad (1)$$



Scheme 1. Schematic illustrations of captures of NH_3 and CO_2 on dendrimer-loaded organoclay adsorbents.

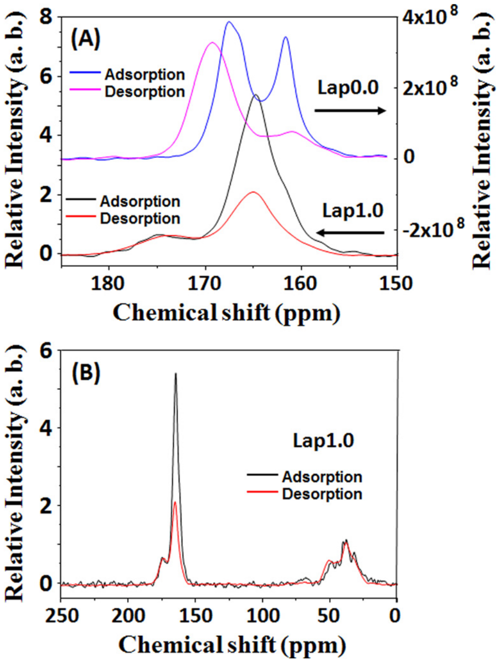


Fig. 5. Solid-state ^{13}C NMR spectra. (A) Pristine laponite (Lap0.0) and laponite organoclay (Lap0.1) recorded after adsorption and subsequent desorption of isotope-enriched $^{13}CO_2$. (B) The corresponding spectra observed for Lap0.1 in full scale.

The sodium bicarbonate then can further react with another sodium silicate on the surface of the clay to form sodium carbonate (Eq. (2)):

$$NaHCO_3 + clay - O^{-}Na^{+} \leftrightarrows Na_2CO_3 + clay - OH \quad (2)$$

Meanwhile, the reaction equilibrium of Eq. (1) inclines to move toward left-hand side (i.e., desorption of CO_2) due to evaporation of H_2O, leading to a decrease in bicarbonate species. Eventually, equilibrium is unbalanced, causing the two resonance signals accountable for bicarbonate (162 ppm) and carbonate (167 ppm) to move further toward upfield (lower δ^{13}C) and downfield (higher δ^{13}C), respectively, and considerable decrease in the bicarbonate signal after the desorption of CO_2.

On the other hand, the ^{13}C NMR spectra observed for the dendrimer-loaded laponite organoclay (Lap0.1) after the uptake of CO_2 revealed a main signal at δ^{13}C of 164 ppm with a much weaker signal at ca. 175 ppm (see Fig. 5A). A weak shoulder peak at 162 ppm was also observed, indicating the presence of bicarbonate species associated with the dendrimer-free adsorption sites [30]. Incidentally, multiple resonances arising from carbons of the amine-terminated PAMAM dendrimer were detected around δ^{13}C of 39 ppm, as can be seen from the full-spectra of $^{13}CO_2$-loaded laponite organoclay (Lap0.1) in Fig. 5B. However, resonance signals responsible for physisorbed $^{13}CO_2$ ($\delta^{13}C = 125$ ppm) [30] and free carbamic acid (160 ppm) [31,32] were nearly invisible in Fig. 5B (likewise, for the $^{13}CO_2$-loaded pristine laponite). Moreover, owing to the broad linewidth observed for the laponite organoclay adsorption system, possible contribution from ^{13}C signal of carbonate species (167 ppm) may not be excluded owing to the highly overlapped resonance signal. Nonetheless, even if the carbonate species did exist, its contribution should be minor or negligible. In any case, the primary signal observed for the $^{13}CO_2$-adsorbed laponite organoclay at 164 ppm may be attributed to the formation of carbamate ($-NHCOO^{-}$) species on terminals of PAMAM dendrimers [31–34], which may be expressed as:

$$CO_{2(g)} + 2\ dendrimer - NH_2 \rightleftarrows dendrimer - NHCOO^{-} + dendrimer - NH_3^{+} \quad (3)$$

Upon desorption of CO_2, the noticeable decrease in carbamate signal and the disappearance of bicarbonate shoulder signal were observed. This indicates that carbamate species is more stable than bicarbonate species, likely owing to the existence of covalent bonds between the nitrogen and carbon atoms [33,34]. Thus, the above results clearly verify that CO_2 adsorbates tend to adsorb preferentially on terminal amines of the loaded dendrimer but less on adsorption sites of the laponite clay.

4. Conclusions

We prepared a series of organoclay adsorbents prepared by surface modification of commercially available clays with PAMAM dendrimers. Then, anion-exchange (hydrotalcite) and cation-exchange (laponite and sericite) clays were loaded carboxylate-terminated (G4.5) and amine-terminated (G4.0) dendrimers, respectively. The adsorption and desorption properties of these organoclay adsorbents were assessed for NH_3 gas and compared to CO_2. The two gases showed the preferred adsorption on different organoclay adsorbents. It was found that NH_3 tended to be selectively adsorbed on anion-exchange hydrotalcite clay loaded carboxylate-terminated dendrimers, whereas CO_2 was preferentially adsorbed on cation-exchange laponite and sericite clays loaded amine-terminated dendrimers. This selectivity can occur by the specific interaction of CO_2 with amine moiety in adsorbents and probably by the similar interaction of NH_3 with carboxylate moiety in adsorbents. The variations of adsorption capacity and selective desorption apparently reflected surface properties of pristine clays and corresponding organoclays. The results reported in this investigation clearly show that organoclay adsorbents can readily be prepared by properly choosing clays having unique surface properties and dendrimers with desirable functional moieties for efficient capture of selected gases. These task-specific, tailor-made organoclays, which may be facilely prepared on a massive scale, indicate prospective industrial applications as efficient adsorbents for gas capture and release. In addition, we should notice that this is the first report of NH_3 gas adsorption on clays and dendrimer-incorporated organoclays as far as we know, although CO_2 gas adsorption on clays and dendrimer-incorporated organoclays has been slightly reported [4,35,36].

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