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High-Pressure Methane, Carbon Dioxide, and Nitrogen Adsorption on Amine-Impregnated Porous Montmorillonite Nanoclays

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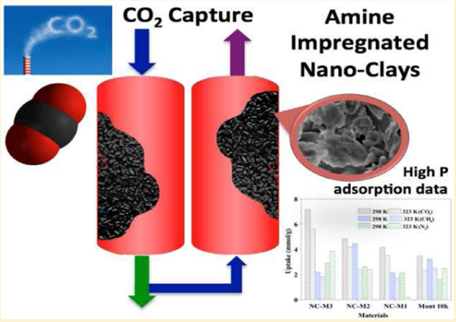
S *Supporting Information*

ABSTRACT: Montmorillonite nanoclay was studied for its capability of storing carbon dioxide, methane, and nitrogen at elevated pressures. Adsorption data were collected to study and assess the possible applications of montmorillonite to gas storage, as it is available in depleted shale reservoirs. The thermodynamic properties of montmorillonite and its amine impregnated structures were studied in this manuscript. Material characterization via Brunauer–Emmett–Teller analysis, thermogravimetric analysis, Fourier transform infrared and energy dispersive X-ray spectroscopies, and scanning electron microscopy was carried out on the nanoclay samples followed by low- and high-pressure gas sorption experimental measurements via high-pressure magnetic suspension sorption apparatus at 298 and 323 K isotherms up to 50 bar. Selectivities of each gas on each nanoclay material is calculated based on single gas adsorption measurements and presented in the manuscript. Additionally, heat of adsorption and kinetics of adsorption are calculated and reported.



1. INTRODUCTION

Atmospheric CO_2 and other greenhouse gases (GHG) levels are rising at a rate that parallels global temperature increases. These emissions, which mostly come from the combustion of fossil fuels such as coal, oil, and natural gas (ca. 80% of CO_2 emissions worldwide), are projected to keep increasing particularly due to economic growth and industrial development in developing nations.[1,2] Therefore, currently there is significant interest in the development and implementation of technologies that reduce CO_2 emissions. The use of amine solvents (e.g., 30% monoethanolamine (MEA) in water) for the absorption of CO_2 is currently the only technique to have been employed commercially for the removal of CO_2 from flue gas.[3,4] The low solvent cost and proven effectiveness make MEA an attractive absorbent for many applications. The main disadvantage of this technology is that these amine solutions contain 70% water by weight, and the regeneration cycle involves heating and evaporating large volumes of water and stripping CO_2 from the solvent, which makes the process extremely energy intensive. Indeed, if MEA were to be utilized for carbon-dioxide capture and sequestration (CCS), electricity prices are projected to increase by 86%.[5] Adsorption-based techniques are promising due to their inherent simplicity, low operational requirements, ease of control, and high efficiency. For these reasons they can be considered as a serious alternative to amine-based CO_2 absorption.

However, owing to high material synthesis and manufacturing costs, moisture sensitivity, material regeneration energy requirements, and low selectivity toward CO_2, most of the novel porous materials that are proposed as alternative acid gas removal agents have not been effectively commercially utilized.[6] In parallel to search for advanced materials for carbon capture and storage, investigations into gas storage on gas shales have been conducted in recent years.[7]

Gas shales are complex rocks, characterized by heterogeneity in composition and structure at all scales. Similarly, the production of natural gas from shales is controlled by phenomena acting at many different scales, as has been reviewed by several authors.[8] One important property that affects the production from shale gas reservoirs is the adsorption of methane, which is affected and controlled by the microstructure, the composition, and the rock slab. By storing the liquid-like adsorbed dense phase of a gas instead of the free phase alone of the gas, the overall storage performance of the rock is enhanced. On the other hand, release of the adsorbed phase is a function of pressure, as the reservoir depletion continues, the adsorbed phase is released and assists to sustain reservoir pressure.

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Table 1. Simple IDs, Types, And Average Quantities of Amine Function Groups Used for Surface Modification of Materials

	elements		
nanoclay type	inorganic	organic	sample ID
montmorillonite K 10 ($H_2Al_2(SiO_3)^{4-}\cdot nH_2O$)	Al, Si	H_2, O_2	MMT
nanoclay, surface modified contains 0.5−5 wt % amino propyl trie thoxysilane, 15−35 wt % octadecylamine, MDL number MFCD00147658	Al, Si	N_2, C, H_2, O_2	MMT-1
nanoclay, surface modified contains 35−45 wt % dimethyl dialkyl (C14−C18) amine, MDL number MFCD00147658	Al, Si	N_2, C, H_2, O_2	MMT-2
nanoclay, surface modified contains 25−30 wt % octadecylamine, MDL number MFCD00147658	Al, Si	N_2, C, H_2, O_2	MMT-3

Clays are natural, earthy, fine-grained materials that develop plasticity when mixed with a limited amount of water. The common clay minerals can be classified into five groups: smectite (montmorillonite, beidellite); illite (illite and glauconite); kaolinite (kaolinite, halloysite); chlorite (chlorite); sepolite (sepolite and palygorskite). Montmorillonite (MMT), widely used as inclusion in polymer nanocomposites, is formed by the weathering of eruptive rock material (usually tuffs and volcanic ash).[7,9] MMT has been considered for several technological applications such as the development of polymer−clay nanocomposites (PCNs) because of the enhancement of thermodynamic and mechanical properties of the polymer upon composite formation.[10]

MMT is a layered silicate, belonging to the 2:1 phyllosilicates family, the crystallographic structure of which is based on the phyrophyllite model. The structure is composed by a central layer of octahedrally coordinated metal (Al^{3+}/Mg^{2+}), sandwiched between two tetrahedrally coordinated layers of silicon. The clay layering allows the delocalization of negative charges, which are balanced by cations such as Na^+ (Na-MMT) placed in between the charged layers.

The sorption of methane and carbon dioxide (and possibly nitrogen) on mineral samples and gas shale and the utilization of MMT were studied by Heller et al.[7] MMT by itself has limited CO_2 sorption capability; therefore, to improve its CO_2 capture capacity and selectivity, several alternative modifications and processes were proposed such as microstructure and morphology control, shale composition and surface modification, and optimization, etc. In particular, impregnating or grafting certain types of solid amines and ILs on the above porous materials has been well recognized, and most promising alternatives consider the potential of amine structures and their affinities especially for CO_2.

Hicks et al. proposed flowing CO_2 containing gas through a bed of amine-modified MMT adsorbent for CO_2 capture previously.[11] On the other hand, Stevens et al. also synthesized diamine impregnated MMT via a water aided exfoliation and grafting route and achieved a CO_2 adsorption capture performance of 2.4 mmol g^{-1} at 100 °C.[12] The maximum CO_2 adsorption capacity in 15% CO_2 in N_2 was 1.8 mmol g^{-1} at 95 °C. On the other hand, Roth et al. modified MMT nanoclay with aminopropyltrimethoxysilane (APTMS) and PEI for CO_2 capture.[13]

Heller et al. also worked with both untreated and amine-modified MMT nanoclays and noted that CO_2 capture performance was considerably increased after the nanoclays were doped with amines, particularly with both APTMS and PEI. They recorded fast sorption kinetics and capture capacities as high as 1.7 mmol g^{-1} at 1 bar and about 3.9 mmol g^{-1} at 20 bar at temperatures around 75 °C, and these materials were proposed for pressure swing operations.[7]

Therefore, considering the previous studies on MMTs modifications for gas adsorption, we report in this work the behavior of three amine-functionalized MMTs in comparison with unmodified MMT regarding carbon dioxide, methane, and nitrogen. The experimental results using a wide collection of methods in wide pressure and temperature ranges allowed a detailed characterization of these materials for shale gas treatment and the effect of amine−functionalization on gas adsorption and selectivity.

2. METHODS

2.1. Materials. Both nonmodified and amine impregnated nanoclay materials were obtained from Sigma-Aldrich and were used for gas sorption measurements capture without any further chemical modification. Abbreviations for the materials are given as montmorillonite (MMT), modified montmorillonites (MMT-1, MMT-2, and MMT-3). Table 1 shows the details of the names and quantity of amine groups that were used for the surface modification of the MMT nanoclays.

3. RESULTS

3.1. Material Characterization. Prior to the experimental gas sorption performance test, nanoclay materials were characterized by using various relevant techniques.

FTIR spectra of the materials were taken via Bruker Vertex 80 spectrometer in the range of 4000 to 400 cm^{-1}. FTIR analysis shown in Figure 1 confirmed the attachment of various amine groups to the structure of nanoclays. The characteristic Si−O−Si bending can be observed with the broad peak at around 1032 cm^{-1}, whereas another broad peak at 3625 cm^{-1} can be assigned to O−H stretching of MMT.[14] The minor peaks at the 3246 region can be attributed to O−H stretching suggesting water traces in the structure. It is important to note that after the amine impregnation, the Si−O in-plane stretching at around 980 cm^{-1} became more intense and a wide peak

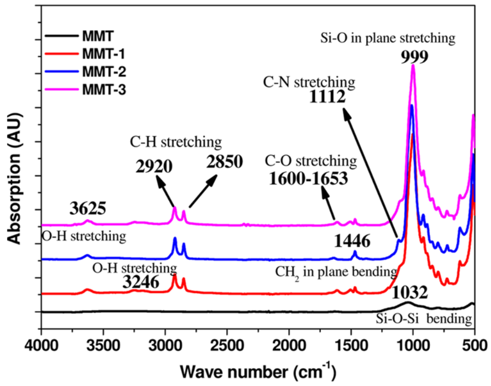

Figure 1. FTIR analysis of nanoclays samples.

between 1146 and 740 cm^{-1} appears indicating the presence of Si−O bonding.[13] The C−H stretching observed at 2850 cm^{-1} to 2920 cm^{-1} and the broad peak at 3300 cm^{-1} can be assigned to N−H stretching from the amine in APTMS. FTIR analysis of all the samples conclude that various amine functional groups have been impregnated onto the structure. Further, a detailed FTIR analysis of modified nanoclay materials, with results identical to our results, can be found in the literature.[15]

Thermal stability investigation was carried out with PerkinElmer Pyris 6 TGA apparatus, for which the materials were heated under a N_2 blanket from 30 to 800 °C with 5 °C/min heating ramp and results are given in Figure 2. Thermal analysis showed that the nonmodified nanoclay sample was stable up to 300 °C; however, there was a 5% loss in the materials weight, which was mainly attributed to the stored water in the materials. The second loss started at around 300 °C, causing a further 4% loss in the material weight, which was associated with the very slow decomposition of nanoclays. It can be deduced from the thermal analysis that the nonmodified material has shown very good stability, due to very low decomposition (8%) when the material was heated up to 700 °C. On the other hand three-step decomposition starting at 270 °C (5%), 400 °C (15%), and 560 °C (35%) was observed in all amine-modified materials. The initial 15% decomposition of modified materials can be associated with the burning of the amine group, whereas the next 35% can be the loss of nanoclays suggesting instability of the material beyond 400 °C. Almost similar findings were observed for all nanoclay materials modified with other organic moiety, such as ethylene glycol.[16] It is important to note that all of the materials have shown good thermal stability up to 270 °C.

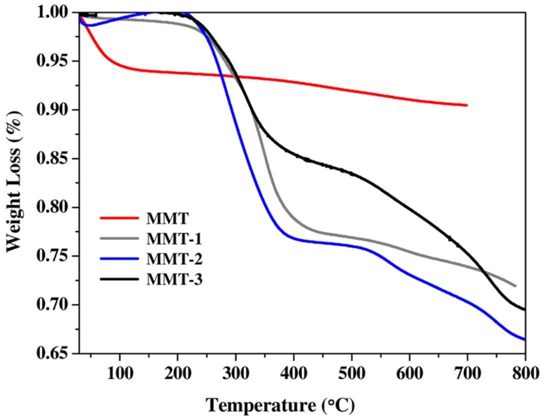

Figure 2. Thermal gravimetric analysis of nonmodified and amine modified samples.

Brunauer−Emmett−Teller (BET) measurement and degassing of the samples were performed with a Micromeritics ASAP 2420 surface and porosity analyzer. Figure 3 and Table 2 show BET analysis of materials conducted with liquid nitrogen. BET surface area and pore volume of pristine nanoclay material are found to be 253 m^2/g and 0.42 cm^3/g, respectively, which are evidently much higher that the modified materials. It can be seen from Table 2 that after impregnation with APTS (aminopropyltriethoxysilane), dimethyl dialkyl amine (DDA), and octadecylamine (ODA), the surface area and pore volume are significantly reduced suggesting incorporation of various amines into the porous structures of the nanoclays. Importantly, amine modification also influenced the density of materials which was reduced up to 70% after modification. Although, the surface area and pore volumes of the materials were reduced significantly, however, it was proven that, affinity of CO_2 enhanced due to the attachment of the function group on the surface and inner pores of the materials. Such effect of reduction in the physical properties but enhancement in the affinity of CO_2 has been reported in the literature in the case of solid sorbents such as mesoporous silica, metal organic framework, activated carbon and nanomaterials.[17−21] Prior to surface area and pore volume measurements, samples were degassed at 150 °C for 5 h under vacuum. The same apparatus was also used for low-pressure gas adsorption measurements, and the findings of those measurements are discussed in section 3.

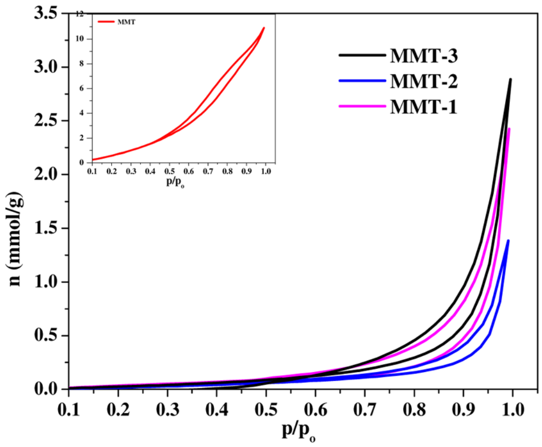

Figure 3. BET isotherms for all nanoclays materials.

Table 2. Physical Properties and BET Analysis of Nanoclays Materials

sample	density (g/cm^3)	pore volume (cm$_3$/g)	BET surface area (m$_2$/g)	pore size
MMT	0.5857	0.42	253.423	6.5
MMT-1	0.4355	0.092	12.286	29.5
MMT-2	0.3685	0.053	8.4743	24.8
MMT-3	0.3408	0.11	11.82	37.0

Elemental analysis for the nanoclays studied by using PerkinElmer 2400 series II CHNS/O system. Table 3 includes the results from the CHNO analysis. Scanning electron microscopy (SEM) analysis is used for initial investigation of the surface morphology. SEM images were captured via Nova Nano SEM 450 produced by FEI, USA, environmental scanning electron microscope (ESEM) with a resolution of 5 nm and a magnification X200 K, equipped with a model BRUKER 127EV detector supplied by Bruker Inc.

Table 3. Elemental Analysis of Organic Compounds, N, H, and C after Modification with Various Amines Groups

sample	N%	C%	H%
MMT	0	0	0.833
MMT-1	1.314	20.636	4.241
MMT-2	0.879	29.286	5.651
MMT-3	1.312	20.786	4.307

Figures 4 shows the morphology and structure of the nanoclay materials. After the modification with amines, the surface of the MMT turned rougher than in MMT with more

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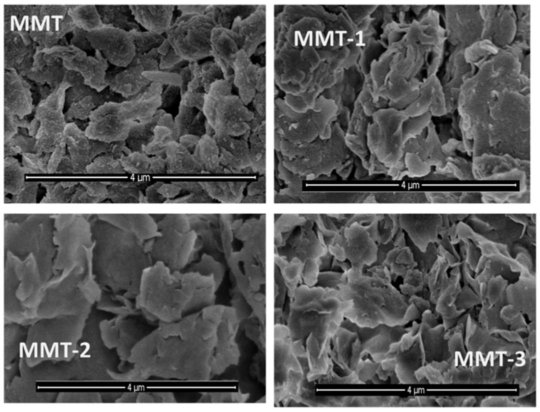

Figure 4. SEM images of modified and nonmodified nanoclays.

fractionated lamellas and particles with the form of flakes; which is quite observable for the MMT-2 sample in Figure 4. These lamellas did not group in an oriented disposition, but formed a mass of particles in a randomized and disordered way. The amount of amine concentration does not have a systematic effect on the pore volumes, but it can be claimed from the SEM images that the surface area and the pore sizes are decreased with the amine modifications of the MMT clay.

Energy-dispersive X-ray spectroscopy (EDX) analysis was also conducted along with the SEM imaging, and the values of C, K, Fe, O, Mg, Si, and Al compositions are plotted in Figure 5

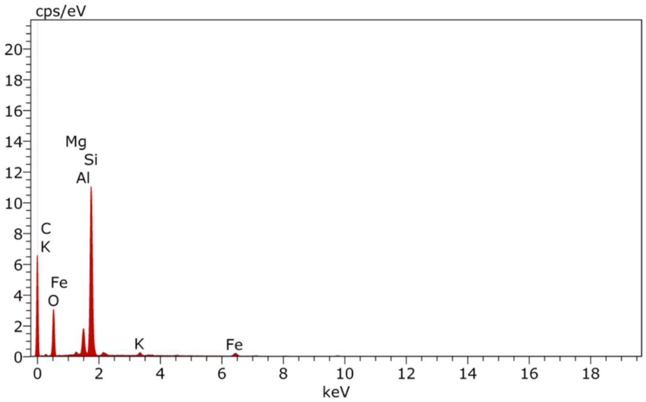

Figure 5. EDX analysis of base nanoclay sample showing inorganic elements.

as a function of concentration. It must be highlighted that despite the surface analyzing capability of EDX, the powdering of the samples rendered them homogeneous and representative in their whole volume. The EDX analysis of MMT-1, MMT-2 and MMT-3 are given in Figures S3−S5 of electronic Supporting Information.

BET analysis was used for low pressure CO_2 uptake; however, magnetic suspension apparatus (MSA) from Rubotherm equipped with automated Teldyne Isco 260D pump was used to obtain the CO_2, CH_4, and N_2 quantity adsorbed by modified and nonmodified nanoclay materials. Details of the experimental set up for high-pressure gas measurement have been mentioned elsewhere.[22−25] In a typical procedure, a known amount (0.10 to 0.2 g) of sample was degassed for 5 h at 150 °C and was then kept in the MSB sample holder for further evacuation at various temperatures as required for 5 h. The maximum set pressure (50 bar) was applied stepwise by increasing the pressure gradually from 1 bar up to 50 bar. Each pressure point took about 75 min to gain the set point of pressure and temperature, record four different sets of measurements and collect the data points. The system is fully automated and the pressure goes to next higher point after completing the previous measurement point. The system was brought to atmospheric pressure subsequently by evacuation through a stepwise reduction of pressure 50 bar to evacuation stage in order to achieve the desorption characteristics of the materials. Details on the findings of the sorption measurements are given in section 3.

Figure 6 shows the X-ray diffraction analysis of MMT (a), MMT-1 (b), MMT-2 (c), and MMT-3 (d) obtained with Cu Kα, emission of 15 mA at the rate of 4 degree/min at room temperature. Figure 6a clearly shows characteristic peaks at (2°θ) 8.88, 26.64, 45.52, 54.84, 61.96, and 73.32 corresponding to the interlayer spacing of the montmorillonite structure. After modification with various amines groups, the interlayer space of the nanoclays was significantly modified as shown in Figure 6b−d. The peak at 3.04 in MMT shifted toward 4.4 in all of the materials; however, it becomes more prominent in MMT-1 and MMT-3, while the concentration of this peak is weak in MMT-2. Additionally, the significant peak of MMT at 26.64 becomes almost negligible in the amine-modified materials, whereas the small peak at around 20.84 of MMT becomes more visible in all modified materials with a little bit lower shift toward 20.04. It is important to note that peaks at around 20, 54, 61, and 73 were common in all of the four materials but with different concentrations indicating the effect of amine impregnation on the structure of the nanoclays.

3.2. Experimental Gas Sorption Results. Figure 7 shows CO_2 adsorption capacities of pristine and amine impregnated montmorillonite materials at two different temperatures and maximum pressure up to 50 bar. The effect of amine impregnation on CO_2 uptake capacity is obvious at room temperature since MMT-3 captures the largest quantity followed by MMT-2 and MMT-1, whereas nonmodified adsorbed the least among all. At a higher temperature of 323 K and pressure above 25 bar, adsorption has almost a similar trend as observed at 298 K; however, at a pressure lower than 22 bar adsorption data is nearly similar for all of the materials. On the other hand at higher pressure, that is, above 25 bar the adsorption isotherms at 323 K for MMT-3 become distinct from the other three materials. A detailed investigation of adsorption isotherms (shown in Figures S1 and S2 of Supporting Information) reveals that MMT adsorbs almost an equivalent or even more quantity of CO_2 in the pressure ranges of 8 and 20 bar at 298 and 323 K, respectively, than amine impregnated materials. This unique behavior can be associated with larger pore volume and surface area of the nonmodified material. We assume that initially the available empty inner pore surface and outer surface areas of all the materials will be occupied by CO_2 molecules at lower pressure. Since, the pristine nanoclay possesses more unoccupied pore volume and surface area than amine-impregnated materials, it will therefore capture comparatively more CO_2 than the other materials. At pressures higher than 10 bar (298 K) and 20 bar (323 K) CO_2 capture will be due mainly to the nitrogen functionalization instead of larger physical parameters.

It is evident from Figure 7 that at higher pressure (i.e., above than 20 bar), CO_2 uptake is independent of the pore volumes and surface areas of the materials even in the case of modified materials. MMT-2 possesses the lowest pore volume and

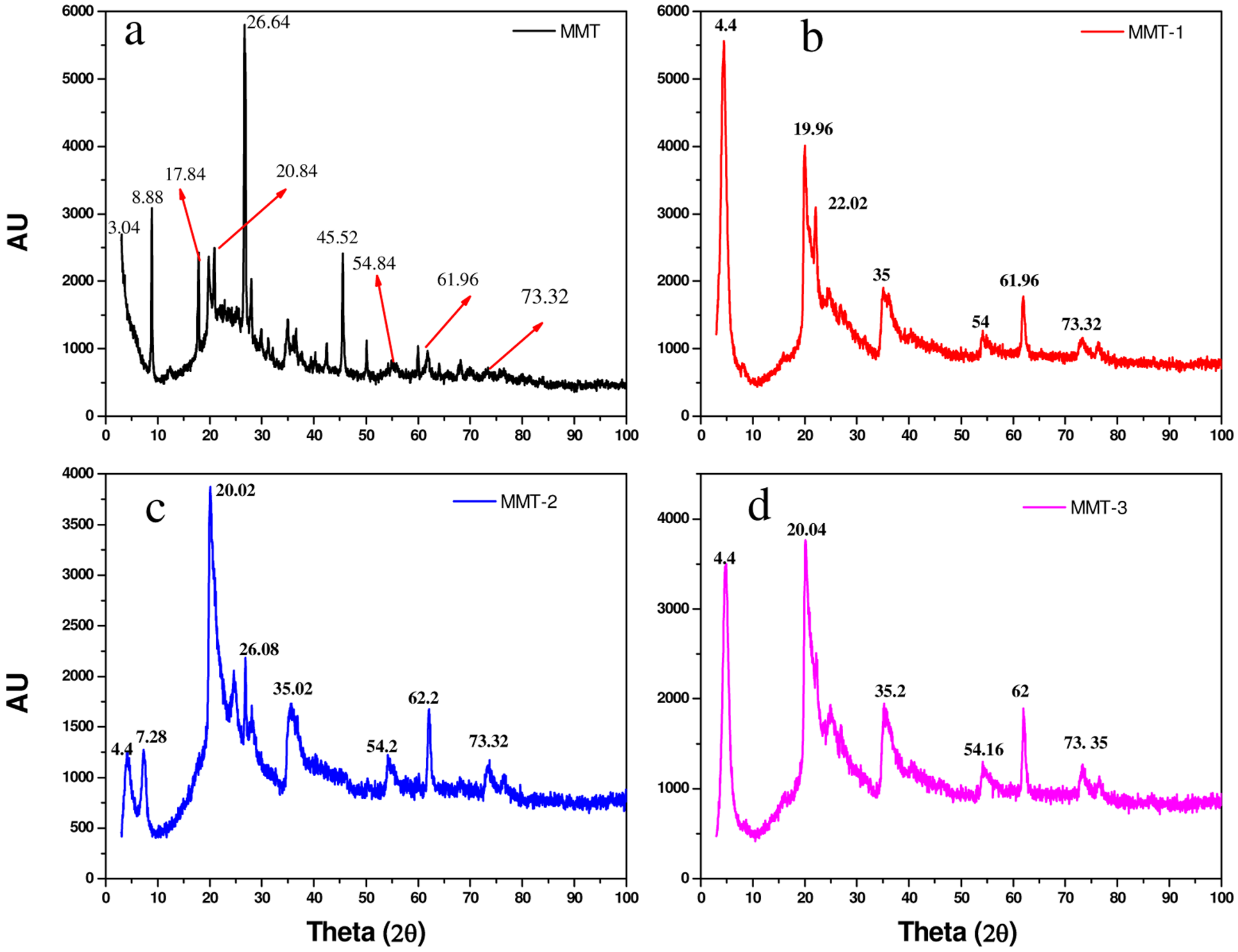

Figure 6. XRD analysis of nonmodified and modified nanocalys samples: (a) MMT, (b) MMT-1, (c) MMT-2, (d) MMT-3.

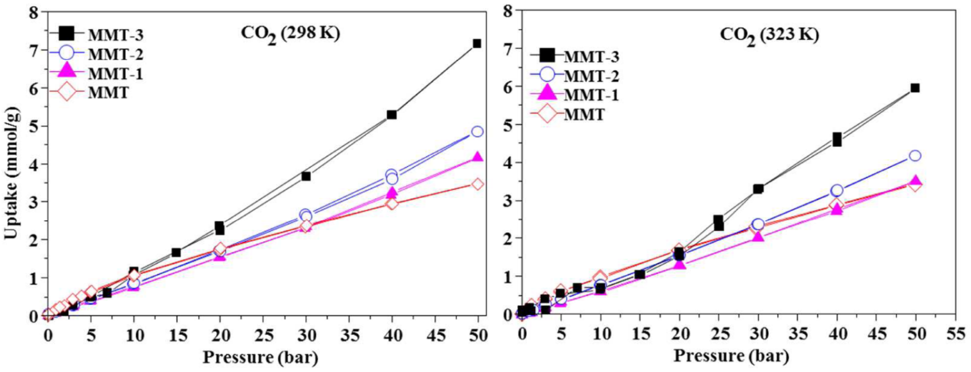

Figure 7. CO_2 uptake by all materials at 50 bar and 298 K (up) and 323 K (down).

surface area, but its adsorption capacity is larger than MMT-1, which has the second largest pore volume and the largest surface area among the amine-impregnated materials. Definitely, the higher CO_2 uptake capacity of MMT-3 among all these materials is attributed to the nitrogen functionalization introduced by otcadecylamine insertion into the pores and on the surface of the nanoclay material. Figure 7 further reveals that impregnation of nanoclays with a single primary amine (otcadecylamine) is more effective than with a tertiary amine (dimethyl dialkyl (C14−C18)) and modification with doubling primary amines, such as octadecylamine and APTMS. Herein we assume that incorporation of a primary amine (octadecylamine) makes nanoclays more hydrophilic by replacing the hydrogen atoms at the two nodes with water or the hydroxyl radicals which in turn increase the number of active sites for CO_2 capture. On the other hand in the case of MMT-2 which was modified with tertiary amine (dimethyl dialkyl (C14−C18)), CO_2 may only be attached via unpaired electrons on the N atom since all the three nodes are already occupied by carbons of the methyl group. Contrary to the above assumptions, in the case of MMT-1, the methyl of one function group (say octadecylamine) may be bonded with the nitrogen of another function group (APTES) by replacing hydrogen and vice versa, resulting in lowering the overall functionality of the modified material. Thus, lower performance of doubly functionalized nanoclays (MMT-1) than the other two counterparts can be the reason for occupancy of possible reactive sites due to the exchange of methyl groups. Additionally, aggregation of two different organic moieties may also adversely affect the accessibility of active sites which subsequently reduces CO_2 adsorption capacity. As shown in Table 3, nitrogen content of MMT-1 is slightly larger than that in MMT-3 but the performance of the latter is comparatively better than the former. Thus, it is not only the concentration of N incorporated into the pores of materials but also functionalization of the induced nitrogen that is important for CO_2 adsorption. Roth et al. also reported that nanoclays modified only with a primary amine (APTMS) have better CO_2 capturing capacity at 50 °C than that modified with a secondary amine (polyethylenimine (PEI)) and doubly impregnated materials.[13] Na-montmorillonite is modified with different types of alcohols ranging from ethylene glycol up to Boltorn dendrimers in order to introduce OH functionality and consequently enhance CO_2 capturing capacity.[16] It was demonstrated that CO_2 uptake capacity was mainly related to the number of OH groups which acted as a main driver for the adsorption process.[26] It is important to note that this alcoholic-based CO_2 adsorption via OH group interaction involves formation of carbonate which subsequently changes the color of the adsorbents[27] indicating a chemisorption process. We utilized the same sample for several runs of CO_2, CH_4, and N_2 adsorption and neither discoloration nor degradation in the performance was observed. Additionally, FTIR analysis of arepeatedly used sample for different gases at different temperatures does not show any extra peaks which may indicate chemisorption of CO_2 or formation of any other compound. Another important aspect of Figure 7 is that unusually CO_2 uptake by nonmodified nanoclays (MMT) is almost similar at both temperatures, while for all modified materials adsorption is higher at lower temperature. Almost similar results of lower adsorption at lower temperature by montmorillonite and SBA-15 have been reported in the literature.[13,28,29] In a recent study by DashtArzhandi et al.[30] porous mixed membranes of polyvinylideneflouride (PVDF) and hydrophobic montmorillonite (MMT) were tested for CO_2 stripping at various temperatures. Results indicated that MMT integrated membranes of PVDF showed an increase in CO_2 stripping with an increase in temperature from 27 to 45 °C and 85 °C, while further increase in temperature was detrimental for the mixture performance. Generally, heat associated with adsorption of gases on solid surfaces suppresses the adsorption process which subsequently results in lower adsorption capacity at higher temperature. Though, in the case of nonmodified material (MMT), we argue that diffusion of CO_2 will be comparatively slower at lower temperature, which in turn requires longer time for the equilibrium to be achieved. On the other hand at higher temperature, diffusion will be faster and the pores of the material will be occupied quickly, which is evident from the rate of adsorption data explained in the following section. Since, the same amount of time was given for the data points to achieve the equilibrium condition at both temperatures during the adsorption process, at lower temperature due to the slower diffusion CO_2 uptake will be lower than that at high temperature for the same time of adsorption. Thomas et al. discussed in detail the effects of length of adsorption time as well as the effect of temperature on the diffusion of CO_2 and suggested that longer time adsorption is advantageous.[31]

Figure 8 shows isotherms of MMT for CO_2, CH_4, and N_2 at room temperature and higher temperature of 323 K and 50 bar.

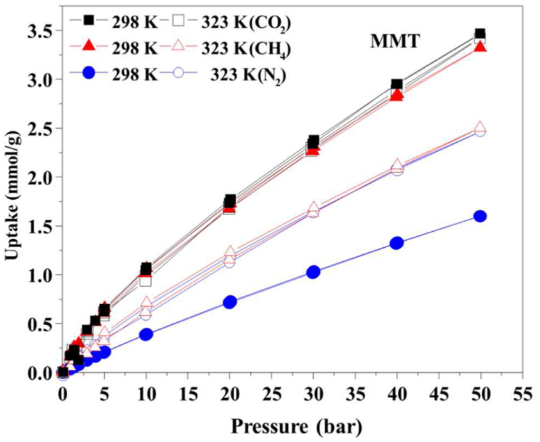

Figure 8. CO_2, CH_4, and N_2 adsorption desorption isotherms of MMT 10 at 50 bar, 298 K, and 323 K.

As discussed earlier CO_2 adsorption by MMT at two different temperatures is nearly similar, whereas there is a significant difference in the adsorption capacity of N_2 and CH_4 at two temperatures. Interestingly, MMT uptakes approximately similar quantities of CO_2 and CH_4 at room temperature, but adsorbs less quantity of N_2 under similar conditions. It is important to note that unlike other solid sorbents MMT captures more N_2 at higher temperature than at lower temperature. MMT adsorption behavior is practically non-comparable to other solid materials at these conditions of pressure and temperature. Since CO_2 adsorption is about similar at the two different temperatures, CH_4 and CO_2 are comparable when captured at 298 K and N_2 uptake increases with increasing temperature. Roth et al.[13] also reported a similar effect of increasing CO_2 adsorption capacity with an increase in temperature up to the maximum of 125 °C for bared montmorillonite. In our case CO_2 adsorption at two temperatures was comparable, but N_2 was increasing with increase in temperature. It has been proven experimentally that, by increasing the temperature, the pore volume and surface area of MMT reduce significantly due to the squeezing of basal spacing and interlamellar space causing structure instability at high temperature.[32,33] The acidic nature of MMT which influences the catalytic properties is strongly structure dependent. Calcination migrates protons within the vacancies between the sheets in octahedrally substituted MMT and leaves the site as a Lewis acid.[34] Decrease in surface area via temperature variation further increases the number of acidic sites.[35] Herein we assume that the increase in acidic sites due to increase in temperature would expedite N_2 interaction with the active sites resulting in a large adsorption capacity of N_2 at higher temperature. N_2 interaction with active sites is more favorable in the acidic environment at higher temperature than at lower temperature due to presence of a quadruple moment on N_2 molecules produced by the partial charges.[36] Thus, at higher temperature, both number of acidic sites on the adsorbent and quadruple moment of N_2 increase which in turn increases adsorption of N_2 at higher temperature.[37]

Figure 9 shows adsorption−desorption isotherms of aminopropyl-triethoxysilane (APTES) and octadecylamine surface modified nanoclays (MMT-1). It is evident from the figure that

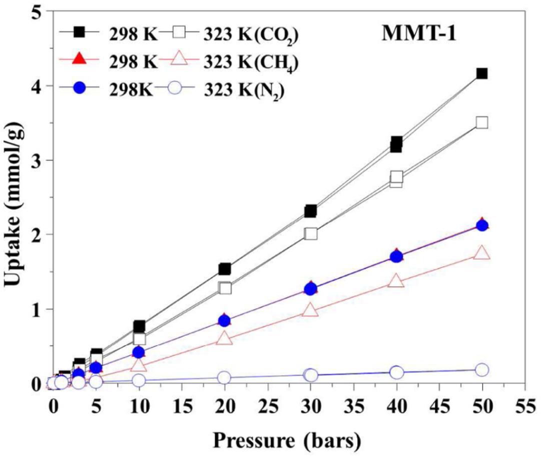

Figure 9. CO_2, CH_4, and N_2 adsorption desorption isotherms of MMT-1 at 50 bar, 298 K, and 323 K.

the behavior of MMT distinctly changed after surface modification with two different types of amines at the same time. CO_2 uptake increases slightly, methane uptake decreases at both temperatures, whereas N_2 adsorption increases at the lower temperature and significantly reduces at the high temperature by MMT-1 as compared to that of MMT. Unlike that of MMT there is a clear difference between the adsorption isotherms of CO_2, CH_4, and N_2 at two temperatures, that is, 298 and 323 K indicating an exothermic effect of temperature on the capturing capacity of the material. MMT-1 possesses the second highest CO_2 capturing capacity at 298 K, the lowest methane capacity at both temperatures, and the lowest N_2 capacity at 323 K as compared to all other materials. Impregnation with two different amine groups shrinks the physical properties such as surface area and pore volume of MMT-1 and induces the largest content of N in the structure as compared to other materials (shown in Table 3). Like other solid sorbents such as SBA-15, activated carbon and covalent organic polymers nitrogen functionalization enhance CO_2 adsorption of montmorillonite owing to the increase of affinity introduced by the inserted function group within the layers of material.[38−40] Unlike TMA- and HDP-modified montmorillonite, N_2 uptake of MMT-1 increases with functionalization of nanoclays at room temperature.[41] This enhancement in N_2 adsorption capacity after impregnation with two different amine groups can be associated with the increase in the interaction of quadruple moment of N_2 with the modified environment. Amine impregnation may increase the columbic interaction between adsorbed N_2 molecules and unpaired N electrons from the amine group which subsequently boosts the capturing process.[42] Figure 9 further reveals that MMT-1 uptakes a similar amount of CH_4 and N_2 at 298 K, while at higher temperature the adsorption capacity of these two gases reduces with different ratios due to the different exothermic properties of the adsorption process. The capturing capacity is strongly dependent on adsorbates, adsorbents types, the way adsorbates interact with the active sites, adsorbents physical parameters, and the affinity of adsorbate molecules toward the capturing sites. Thus, each gas behaves independently when subject to the adsorption process under various temperature and pressure conditions.[41]

Figures 10 and 11 compare the adsorption capacities of dimethyl dialkyl (C14−C18) amine and octadecylamine impregnated nanoclays, respectively. Figure 12 displays the overall performance of all the materials for CO_2, CH_4, and N_2 adsorption capacity. It is evident from these figures that both MMT-2 and MMT-3 capture more CO_2 than the other two gases at room temperature with the exception that MMT-2 uptakes significantly higher quantity of CH_4 at room temperature which is nearly comparable to the quantity of CO_2. In the case of MMT-2, a small decrease in the adsorption capacities of

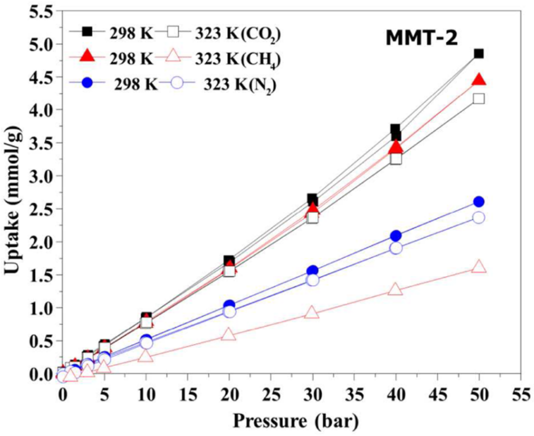

Figure 10. CO_2, CH_4, and N_2 adsorption desorption isotherms of MMT-2 at 50 bar, 298 and 323 K.

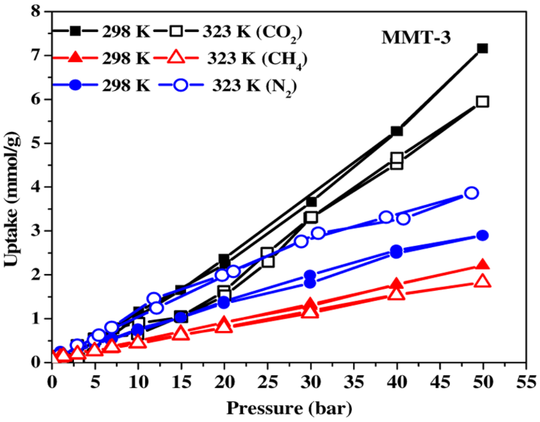

Figure 11. CO_2, CH_4, and N_2 adsorption desorption isotherms of MMT-3 at 50 bar, 298 and 323 K.

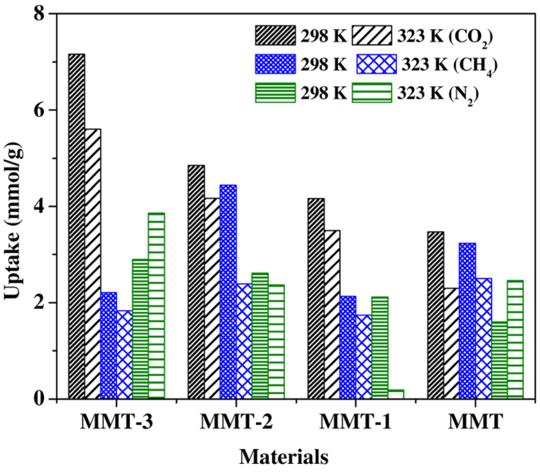

Figure 12. Overall performance of all the materials for CO_2, CH_4, and N_2 adsorption capacity at 50 bar, 298 and 323 K.

CO_2 and N_2 can be observed due to temperature increase, while CH_4 uptake significantly reduces at the higher temperature of 323 K. This considerable reduction in CH_4 adsorption capacity at elevated temperature can be the reason for the unusual increase in the heat of adsorption of MMT-2 as shown in Figure 13 in the case of CO_2. We assume that at higher temperature the heat of adsorption associated with CH_4 adsorption at 323 K would be high enough to hinder further physical attachments of CH_4 molecules thus resulting in a lower capturing capacity at higher temperature. Additionally, diffusion and physical bonding of methane with the active sites would be energetically unfavorable at high temperature, since the physiochemical properties of solid sorbents significantly influence the adsorption process.[42]

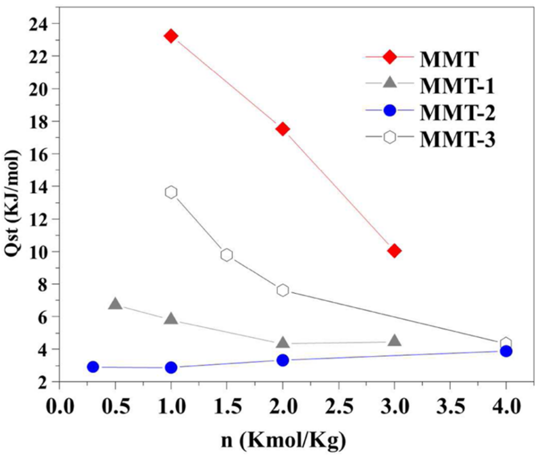

Figure 13. Heat of adsorption associated with adsorption of CO_2 for all nanoclays.

It is important to note that adsorption isotherms of all the gases at all temperatures linearly vary with increase in pressure, which indicates an almost uniform effect of pressure increment on the adsorption process of MMT-2. As seen in Figure 10 octadecylamine-modified material (MMT-3) behaves differently than other modified and nonmodified materials, since it uptakes more N_2 than CO_2 and CH_4 at 323 K and up to the pressure of 25 bar. By increasing pressure beyond 30 bar a rapid increase in CO_2 adsorption was attained at both temperatures, while N_2 and CH_4 uptake was almost approached saturation under similar conditions. Additionally, a minor glitch in CO_2 adsorption at 323 K at the pressure range of 10−25 can be mainly associated with the equipment malfunctioning at this particular pressure range. To avoid such malfunctioning the experiment was repeated about 5 times; however, the abnormal behavior of CO_2 isotherm at 323 K persisted. Under these particular pressure and temperature conditions pore collapse and/or swelling of material may also be a reason causing reduction in the CO_2 adsorption and lowering the diffusion of adsorbate molecules. A recent investigation has indicated an instantaneous decrease in the porosity of montmorillonite which has subsequently caused reduction in the permeability of coated and noncoated materials.[43]

It must be noted that irrespective of the adsorbate gases and under any condition all the materials nearly have reversible isotherms with very negligible hysteresis in the case of only CO_2 adsorption by MMT-2 and MMT-3 at 298 K. A slight hysteresis between 20 and 45 bar both in MTT-2 and MMT-3 observed only for CO_2 can be associated with the difference in the delay during detachment of adsorbate molecules from the interior and exterior of modified pores. It is important to note that in the case of MMT-2 and MMT-3 both adsorption isotherms of CO_2 are practically linearly dependent on pressure; that is, adsorption capacity is increasing with increase in pressure demonstrating suitability of these materials for high-pressure adsorption applications. At this stage the adsorption isotherms obtained up to the pressure of 50 bar may be hardly associated with IUPAC nomenclature; however, further increase in pressure may saturate the material and make the isotherms like those of type IV indicating small adsorbate−adsorbent interaction. The trend in adsorption isotherms of MMT-2 is CO_2 > CH_4 > N_2 at 298 K, which changes to CO_2 > N_2 > CH_4 at the high temperature of 323 K. Such trends in adsorption capacities of different gases have been observed for activated carbon and SBA-15 at different temperatures and pressures.[28,44] On the other hand for MMT-3 the trends of isotherms is CO_2 > N_2 > CH_4 which is identical at both the temperatures and resembled to the trend (of these gases based on) the molecular simulation for the zeolites as solid sorbents.[36] The higher uptake of N_2 than CH_4 was regarded to be the effect of smaller molecular size of N_2 (3.646 Å) than CH_4 (3.76 Å).[45] Conversely, we argue that the affinity of N_2 toward MMT-3 would be higher than that of CH_4 which is further increasing with increase in temperature, eventually increasing N_2 adsorption capacity at higher temperature, as can be seen in Figure 10. A similar effect of higher N_2 uptake than CH_4 by montmorillonite has been observed in amorphous and pillared nanoclay materials indicating the effect of affinity rather than the molecular size.[46] The better CO_2 adsorption capacity of MMT-3 than MMT-2 at both temperatures can be attributed to the differences between the functional group introduced within the pores and the layers of nanoclays. We assume that insertion of octadecylamine in montmorillonite creates more active sites by replacing some cations within the layers with organic moieties and enhances the attraction strength due Van der Waal and Columbic interactions between the adsorbate and adsorbent which consequently increases CO_2 adsorption capacity. Additionally, insertion of some function group within the pores of solid sorbents causes them to become positively charged and they then interact with the partially negatively charged O_2 of CO_2 resulting in the capture of adsorbate molecules.[47−49] It can be suggested that the functional group associated with the N of otcadecylamine sustains larger positive charges than other functional groups, which attracts more CO_2 molecules; therefore, MMT-3 captures a larger quantity of CO_2 than MMT-2 and all other materials.

Figure 12 shows the overall performance of all the materials for three gases at two different temperatures and maximum pressure of 50 bar. It is evident from the bar chart that MMT-3 uptakes the highest quantity of CO_2 at both temperatures followed by MMT-2 and MMT-1, and nonmodified uptakes the least among all the materials. Interestingly, as we discussed earlier in detail MMT-3 also uptakes less N_2 than CH_4, and MMT-2 and MMT capture more CH_4 than CO_2 although at different temperatures. The only significant difference in the highest adsorption capacity of gases can only be observed in MMT-3 followed by MMT-2, since both were impregnated with otcadecylamine. Importantly, MMT-1 captures the least N_2 at 323 K and 50 bar but at the lower temperature of 298 K it adsorbs a similar quantity of CH_4 as N_2 which indicates the impracticality of this material for gases separation purposes. Nevertheless, upon comparing the adsorption capacity of these

Table 4. Summary of Adsorption Performance of Nanoclays for (CO_2, CH_4, N_2) Gases at 50 bar and at Two Isotherms (298 and 323 K) along with Selectivity

	sorption capacity (mmol of gas/g of sample)						selectivity[a]	
	CO_2		CH_4		N_2		CO_2:CH_4:N_2	
material	298 K	323 K	298 K	323 K	298 K	323 K	298 K	323 K
MMT	3.47	3.42	3.23	2.50	1.6	2.46	2:2: 1	1:1: 1
MMT-1	4.16	3.5	2.13	1.74	2.12	0.18	2:1: 1	19:10:1
MMT-2	4.85	4.17	4.44	2.39	2.61	2.37	2:1: 1	2:1: 1
MMT-3	7.16	5.6	2.21	1.83	2.9	3.86	3:1: 1	3:1: 2

[a] Selectivity values are calculated based on the pure single gas measurement ratios, and the ratio values are rounded to the closes decimal point.

modified materials to that of other nanoclays we found that these types of materials have tested for the first time at these particular conditions and the findings presented here cannot be compared with other similar literature. However, some other modified and nonmodified nanoclays have been tested for adsorption of various gases at low pressure and low temperature.[26,30,50−56] Montmorillonite intercalated with tetramethylammonium (TMA) and hexadecylpyridinium (HDP) cations captured about 0.477 mmol/g CO_2 and 0.065 mmol/g N_2 at 298 K and 1 bar, which was much higher than that adsorbed by untreated MMT. The higher uptake by intercalated MMT was mainly attributed to the increase of d(001) spacing due to insertion of TMA molecules.[41] Volzone et al.[46] reported that amorphous montmorillonite clay minerals adsorbed 0.2 mmol/g CO_2, 0.031 mmol/g N_2, and 0.02 mmol/g CH_4 at standard temperature and pressure. CO_2 adsorption capacity was further increased to 0.284 mmol/g by exchanging cations in amorphous kaolinite derivatives.[57] Additionally, acid treatment increases the pore volume and surface areas of these minerals by leaching octahedral layer cations which causes an increase in gas retention.[58] It is important to note that intercalation of octadecylamine into the layers of montmorillonite nanoclays introduces octadecylammonium stearate which further destabilizes the structure of modified materials. For example, as can be seen in Figure 6a peak at angle 20.04 becomes more prominent in modified materials as compared to that of MMT. Similarly the angle at 3.04 in MMT shifted to 4.4 in all modified nanoclays and becomes more visible in MMT1 and MMT3. Consequently, a gradual rearrangement of the interlayer space brings changes to the structure and makes it unstable even at standard temperature and pressure.[59] Other solid sorbents such as pristine activated carbon and zeolite however uptake about 6.7 and 4.2 mmol/g of CO_2 at 303 K and 7 bar, respectively, which is less than that recorded for MMT-3.[44,60,61] It can be deduced that montmorillonite modified with octadecylamine exhibited better CO_2 capture capacity as compared to all modified nanoclay samples as well as commercial adsorbents such as activated carbon and zeolites.

Selectivity of adsorbents has as similar importance as capture capacity, thus binary selectivity of all the materials based on the maximum uptake at different temperatures has been calculated and given in detail in Table 4. It is important to note that MMT has very poor selectivity for CO_2:CH_4:N_2 at room temperature, which is further reduced to almost null at the high temperature of 323 K. This means that nonmodified montmorillonite adsorbed almost a similar amount of different gases at higher pressure and higher temperature. Interestingly, MMT-1 has the largest selectivity of 19:10:1 over nitrogen at the higher temperature followed by MMT-3 which has six times lower selectivity than MMT-1 but is higher than all other materials.

Figure 13 shows heat of adsorption associated with adsorption of CO_2 on four materials discussed in this article. The isosteric heat of adsorption was calculated with the help of Clausius−Clapeyron using the CO_2 uptake data at different temperatures.[28] MMT possesses the largest heat of adsorption followed by MMT-3 and MMT-1, whereas MMT-2 has the least adsorption heat among all the materials, but it increases gradually as more CO_2 is captured by the material. The maximum heat of adsorption recorded here was found to be around 24 kJ/mol for MMT, which is much lower than that determined for activated carbon (29 kJ/mol), polymers (28 kJ/mol), and zeolite (36.0 kJ/mol);[44,62] however, this adsorption heat is larger than that discovered by us for amine-impregnated and nonmodified SBA-15.[28] During the adsorption process CO_2 molecules move from a high energy state to lower energy state upon adsorption by the active sites of adsorbent, releasing a certain amount of inherited energy in the form of heat, thus increasing the temperature of the surroundings. In nonmodified nanoclays material adsorption process is taking place at the expense of larger energy because the adsorption sites in MMT are less attractive as compared to the adsorption sites of modified materials. Thus, during the physical attachment of adsorbate molecules on pristine material CO_2 molecules release more energy in the form of heat as compared to the attachment of adsorbate onto the amine-activated site in modified materials. We believe that amine impregnation facilitates the adsorption process mainly by increasing the number of active sites due to the presence of N functionality and by intensifying the van der Waal interaction due to the enhancement of electric charge of the active sites.[47,49] It is evident from the figure that with the exception of that for MMT-2, the heat of adsorption is reducing for all materials with an increase in the amount of adsorbate molecules captured by the adsorbents. Similar to that in the literature[62,63] the observed reduction in the adsorption heat can be the reason for a decrease in the diffusion process. Herein we assume that as long as the quantity of adsorbate increases on the attractive sites molecules will diffuse slowly and will cover less distance to be physically bonded onto the site, which consequently liberates a lower heat after adsorption. Heat of adsorption associated with the nitrogen-rich networks is usually higher than that of the nitrogen-free adsorbents suggesting chemisorption and/or strengthens the binding of adsorbate on sorbents.[64] Conversely, in the case of modified nanoclays the heat of adsorption is lower than that of the pristine material which is advantageous as long as regeneration of the sorbent is a concern. All the modified nanoclays can be easily regenerated and can be used repeatedly without high energy penalty. Unlike that of the other three materials, an increase in the heat of adsorption of MMT-2 with an increase in the adsorbed quantity of CO_2 can be associated with the

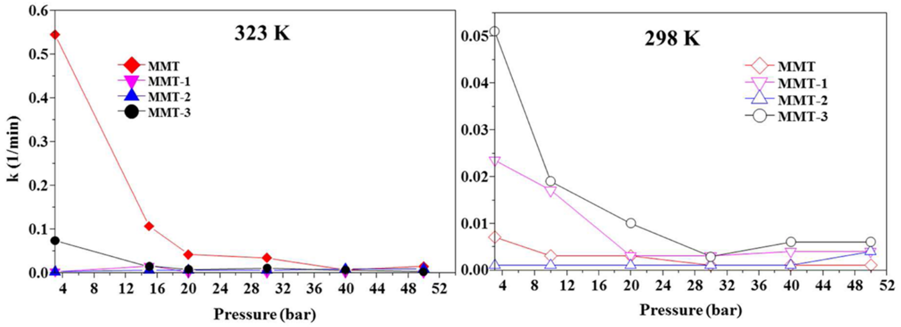

Figure 14. CO_2 adsorption rate of all the materials at 298 and 323 K.

nonhomogeneity of the pores and exterior surface.[65] It can be assumed that impregnation with dimethyl dialkyl (C14−C18) amine may adversely change the interior and exterior of the porous structure, making the material more heterogeneous which subsequently affects the moment of adsorbate molecules during the adsorption process.[66] Thus, as long as the adsorbed quantity increases the favorable interaction of adsorbate increases, which consequently increases the adsorption heat for CO_2 on MMT-2.

Figure 14 shows the rate of CO_2 adsorption of all materials calculated at two different temperatures with the help of the method used in the literature based on adsorption data obtained from a magnetic suspension balance.[66] As shown in the figure, the mass transfer coefficient k (min^{-1}) is the highest for nonimpregnated material followed by that for MMT-3 and MMT-1, whereas MMT-2 has the lowest rate of adsorption at 323 K. Excluding MMT-1, the mass transfer coefficient increases with an increase in temperature for all materials. It can be seen that rate of adsorption of MMT at 298 K is around 0.008 min^{-1} which considerably increases up to 0.55 min^{-1} at the higher temperature of 323 K. This increase in the mass transfer coefficient of CO_2 at an elevated temperature suggests that although adsorption at higher temperature is not favorable owing to the reduction of capturing capacity, the adsorption rate becomes faster at higher temperature. This property of rapid adsorption may be useful in some conditions where gas reactions can be avoided with the help of faster separation and/or adsorption. Additionally, among the modified materials MMT-3 has a larger mass transfer coefficient than the other two modified materials at both temperatures. This further suggests that MMT-3 has the best CO_2 capturing capacity than all other materials, possessing better heat of adsorption that is lower than that of MMT and can more quickly capture CO_2 molecules than the other two modified materials. Generally, for all the materials at every temperature mass transfer coefficients are higher at lower pressure values and then the mass transfer becomes slower gradually as the pressure increases, indicating pore filling of materials upon increasing the pressure. It must be noted that at around 25 bar mass transfer coefficients become flat, independent of temperature with increasing pressure; that is, no further reduction and or increase in the mass transfer can be observed at high pressure. Such an effect of slower mass transfer at elevated pressure has been observed for modified activated carbon and other materials.[29,66,67] Initially, pores are empty and the entire space is available for the adsorbate to be accommodated within the porous structure, thus the adsorbate molecules speedily occupy the space resulting in the faster rate of adsorption at the initial stages. After the initial pore filling process, the moment of adsorbates becomes slower due to the already occupied pores; however, multilayer accommodation continues as long as pressure increases resulting in a flat rate of adsorption with respect to pressure as indicated in Figure 14.

4. CONCLUSIONS

It can be concluded that montmorillonite nanoclays were successfully functionalized with different amine groups via sodium cations exchange techniques, and their gas uptake capacities under various temperature and pressure conditions were evaluated. Elemental analysis and CNHS investigation of pristine and impregnated materials confirmed the exchange of sodium cations with C, N, and S. Thermal gravimetric analysis also indicated that after functionalization, the thermal stability of montmorillonite is significantly reduced because of the exchange of metal cations with organic molecules. Physical parameters such as pore volumes, pore sizes, and BET surface areas of modified materials were also extensively reduced displaying the effect of organic doping and intercalation of functional groups within the layers and pores of the materials. After amine impregnation all the materials were subjected to CO_2, CH_4, and N_2 adsorption under various pressure and temperature conditions to evaluate the adsorption capacity, selectivity, and suitability of these modified materials for gas capture and to separate and compare the outcomes with other counterparts.

Gases capture results obtained with a state of the art magnetic suspension balance (MSB) from Rubotherm reveals that MMT (nonmodified montmorillonite) uptakes the lowest CO_2 (3.47 mmol/g) at room temperature and 50 bar, whereas MMT-3 which was impregnated with octadecylamine captured almost twice the CO_2 (7.16 mmol/g) under similar conditions of pressure and temperature. It must be noted that the other two materials MMT-1 and MMT-2 also adsorbed more CO_2 than MMT at room temperature and 50 bar. This high adsorption capacity of modified materials over that of pristine nanoclays clearly indicates the effect of amine impregnation on the material performance. It was observed that, at the higher temperature of 323 K, the maximum amount of CO_2 adsorbed was slightly reduced owing to the exothermic process for all the materials. Interestingly MMT-3 adsorbed more N_2 than methane at both temperatures (298 and 323 K), whereas MMT-2 uptakes almost similar amounts of CO_2 and CH_4 at 298 K; however, at higher temperature methane uptake was smaller than N_2 for MMT-2. MMT-1 which was impregnated with two different types of amine groups uptakes gases with the trend as $CO_2 > CH_4 = N_2$ at 298 K and 50 bar while at 323 K its uptake trend changes to $CO_2 > CH_4 > N_2$. Although, it was expected that due to the presence of two functionalities (N, S) MMT-1 may have higher adsorption capacity, doubling functionalization was not useful for the capturing capacity and enhanced selectivity. The higher performance of MMT-3 with respect to the adsorption capacity, low heat of adsorption, and high rate of adsorption (at low room temperature) was attributed to the effect of primary amines. It was assumed that intercalation of primary amines within the layers of montmorillonite may be more effective to capture a large quantity of CO_2 than the secondary amine and doubling of the amines groups. The rate of adsorption or in other words mass transfer coefficient k (k $\min^{-1}$) calculated at two different temperatures suggests that MMT-3 uptakes CO_2 more quickly than all other materials at lower temperature, while at higher temperature nonmodified material has better performance followed by MMT-3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.6b00134.

> CO_2 adsorption at low pressure up to 10 bar and 298 K, 20 bar and 323 K; EDX analysis plots for MMT-1, MMT-2, MMT-3; and XRD analysis plots for MMT, MMT-1, MMT-2, and MMT-3(PDF)

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Notes

The authors declare no competing financial interest.

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