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**Synthesis of zeolite/carbon nanotube composite for
gas separation**

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Draft

Abstract

A hybrid composite of NaY zeolite and amine modified multi walled carbon nanotube (MWCNT) has been synthesized by hydrothermal method. The obtained NaY/CNT composite (NC composite) was characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM) and BET analysis. CO₂, CH₄ and N₂ adsorption at two different temperatures and $P < 5$ bar on the composite was investigated by the volumetric method. The selectivity of the NC composite for CO₂/CH₄ and CO₂/N₂ has been studied and compared with pure NaY zeolite. Crystal structures of NC composite were similar to those of pure NaY zeolite, but the surface area and pore volume of the NC composite are enhanced. Incorporation of MWCNTs into NaY zeolite increases nucleation sites for the formation of NaY zeolite crystals, resulting in the smaller size of NaY zeolite crystals. Gas adsorption capacity and selectivity of NC composite increased because of enhancement of micropore volume. The results confirm that NC composite is a promising material for the separation and purification of gases.

Key words: Carbon nanotube, Zeolites, Composite, Adsorption, Gas separation.

48 Introduction

49 Carbon dioxide is the main greenhouse gas that released to the environment as a result of fossil fuel
50 combustion. Currently, natural gas is used as an environmentally friendly fuel compared with other hydrocarbon
51 fuels. In year 2010, natural gas has provided 23.8 % of world total energy consumption and it is predicted to
52 grow by 50 % up to 2040.¹

53 Natural gas is composed mainly of methane (80-95 %), but can also contain varying amounts of undesirable
54 components such as heavier hydrocarbons, carbon dioxide, nitrogen and H₂S. For prevention of equipment and
55 pipeline corrosion, the CO₂ and N₂ concentrations must not exceed 2% and 4%, respectively.² Therefore,
56 removal of CO₂ from CO₂/CH₄ mixture is very important in chemical and petrochemical industries. Moreover,
57 the separation of CO₂ from N₂ in the flue gas (post-combustion) and also the removal of CO₂ from hydrogen
58 (pre-combustion H₂/CO₂), reduces the emission of CO₂ in the atmosphere.

59 Utilization of adsorption based methods in separation and purification of various gas mixtures is promising
60 for reduction of CO₂ emission. Diverse porous materials, such as porous carbon,^{3,4} activated alumina,^{5,6} metal
61 organic frameworks (MOFs),^{7,8} and zeolites^{2,9} have been utilized for this purpose. Among adsorbents, zeolites
62 due to their high adsorption capacity and selective CO₂ adsorption are appropriate adsorbents for CO₂
63 adsorption and separation. Moreover zeolites are cost-effective and have high hydrothermal stability. So far
64 zeolites have been widely utilized as adsorbents for separation of different gas mixtures.¹⁰⁻¹⁷

65 The adsorption capacity of zeolites, surface area and pore volume can be increased by their modification.
66 Common modifications of zeolites for improvement of adsorption capacity are incorporation of amine groups
67 into their structure¹⁸⁻²⁰ and employing different metal ions.^{21,22} A few articles about the synthesis of the
68 carbon/zeolite composite materials have been reported with enhanced porosity and adsorption capacity.²³⁻³⁰
69 Some works have been reported on incorporation of CNTs into MOFs and their effect on adsorption
70 performance.³¹⁻³⁶ However, there are no reports about the incorporation of CNTs into zeolite structures and their
71 effect on porosity and adsorption capacity of CNT /zeolite composite. Due to low hydrothermal stability of
72 MOF materials at high temperatures and cost-effectiveness of zeolites, in this work, we have synthesized the
73 NaY/CNT composite (NC composite) and investigated its efficiency in the improvement of the CO₂ adsorption
74 capacity and selectivity of CO₂/CH₄ and CO₂/N₂. Characterization of these materials was done by X-ray
75 diffraction (XRD), Fourier transform infrared (FT-IR), Brunauer–Emmet–Teller (BET), and scanning electron
76 microscopy (SEM) analysis. Gas adsorption capacity was measured by volumetric method and also effect of
77 rising temperature on adsorption capacity and selectivity of the composite has been studied.

78 Experimental

79 Materials

80 Commercially available MWCNTs, with the purity of around 95% were supplied by Neutrino Co. in Iran.
81 The inner and external diameter of MWCNTs was in the range of 5–10 nm and 10–20 nm, respectively. The
82 specific surface area of MWCNTs was $> 200 \text{ m}^2/\text{g}$. For pre-treatment of MWCNTs prior to functionalization,
83 Sulfuric acid (95–97%) and nitric acid (65%) were used as obtained, without further purification. 3-
84 aminopropyltriethoxysilane (APTES) (purity: $>98\%$, Merck) was used for the functionalization of MWCNTs
85 with amine groups. The materials utilized to prepare the zeolite were fumed silica (SiO_2 63% 200 mesh, China),
86 sodium aluminate (Merck), sodium hydroxide ($\text{NaOH} > 99.999\%$, Merck), and deionized water. The solvents
87 used in this work were methanol and ethanol obtained from Merck. CO_2 , CH_4 and N_2 gas cylinders with purity $>$
88 99.999 were used in adsorption experiments.

89 Synthesis of NaY zeolite and NaY/CNT composite

90 NaY zeolite was synthesized by the following procedure. A reaction mixture with a molar composition of
91 $\text{Al}_2\text{O}_3: 3 \text{ Na}_2\text{O}: 5 \text{ SiO}_2: 200 \text{ H}_2\text{O}$ was made. To prepare aluminosilicate gel, an aluminum gel (solution 1) and a
92 silicone gel (solution 2) were prepared separately. Solution 1 was prepared by dissolving 2 g sodium aluminate
93 in 8.79 g of deionized water. In solution 2, 3.665 g fumed silica and 1.952 g sodium hydroxide were dissolved in
94 33.174 g of deionized water. Solution 1 was mixed with solution 2 in a polypropylene beaker. The prepared
95 reaction mixture was stirred by a magnetic stirrer at ambient temperature for 3 days, and then the mixture was
96 put into a Teflon-line autoclave and heated at 373 K in an oven for 12 h. After the performance of hydrothermal
97 crystallization reaction, the NaY zeolite powders were filtered and dried in an oven.

98 Before the synthesis of NaY/CNT composite, MWCNTs were pre-treated and functionalized by amine
99 groups. In the way that, first MWCNTs were stirred with a mixture of concentrated H_2SO_4 and HNO_3 (3:1, v/v)
100 at 80 °C for 6 h, and then filtrated and washed with deionized water for several times, and dried at 50 °C. Then,
101 the carboxylated MWCNTs (MWCNTs-COOH) after dispersing into flasks containing APTES solution
102 (APTES: ethanol of 1:9, v/v) was sonicated for 6 h and stirred at ambient temperature for 72 h. The mixture was
103 filtered through 0.2 μm fiber filters and washed repeatedly with ethanol and deionized water to remove any
104 residual APTES. Then the filtered solid was dried in an oven at 100 °C for 6 h and denoted as N-MWCNT.

The NC composite was also prepared under the similar hydrothermal procedures of NaY, except various amounts of N-MWCNT were well dispersed in 33.174 g of deionized water of solution 2 and sonicated for 2 h, and then fumed silica and sodium hydroxide were added. The various amounts of N-MWCNT was used to synthesize 15 wt% MWCNT incorporated NaY sample. The synthesized NaY/CNT composite is named as NC composite.

Characterization

The XRD patterns of NaY zeolite and composite were obtained with a powder X-ray diffractometer (Philips PW 1830 X-ray Diffraction) with Cu-K α radiation source. The FT-IR experiments were performed by DIGILAB FTS 7000 spectrometer. The sample powders were mixed with KBr using a mortar and pestle, then pressed into the pellets by a manual pelletizer. The morphologies of the synthesized NaY zeolite and NC composite were identified using a KYKY-EM 3200 field emission scanning electron microscope. The porosity properties of the samples were determined by the nitrogen adsorption–desorption isotherms at 77 K using a micromeritics model ASAP 2010 sorption analyzer. The specific surface area (SSA) was calculated by Brunauer–Emmett–Teller (BET) method.

Gas adsorption measurements

The CO₂, CH₄ and N₂ adsorption isotherms at 298 K were measured by using a laboratory setup based on a volumetric method which has been schematically shown in Fig. 1. In the beginning, 0.5 g of adsorbent was poured into the adsorption reactor and then attached to the system. To ensure that there is no leak in the connections, the system was checked with the inert Helium gas flow. In order to degas the system, the valves 6, 7, 8 and 9 were opened and other valves were closed. Then, the system was vacuumed by the vacuum pump for 1.5 h at 120°C. After degassing the adsorption system, the temperature was decreased to the experiment temperature. To perform the adsorption test, we opened the valves 1, 3, 5, 6, 7 and 8 while other valves were closed. The pressure drop observed during the process was the result of gas adsorption and some dead volumes in the reactor. We could exactly measure pressure reduction relevant to the gas adsorption by measuring the dead volumes via a helium test. The CO₂, CH₄ and N₂ used for the experiment were of 99.99 % purity.

Figure 1

Results and discussion

Adsorbent Characterization

The crystal structures of NaY zeolite and NC composite are identified by XRD. As shown in Fig. 2, the XRD pattern of the NC composite is in perfect agreement with that of NaY zeolite, indicating that MWCNT incorporation does not destroy the formation of the crystal structure of NaY zeolite. Furthermore, in the composite, the weak peak of CNT at $2\theta = 26^\circ$ cannot be observed because of its overlapping with high-intensity peaks of NaY zeolite. Also, after the incorporation of MWCNTs, peak intensities of the composite are higher, indicating that crystallinity of NaY zeolite crystals in NC have improved compared with pure NaY zeolite.

Figure 2

Fig. 3 shows the FT-IR spectra of NaY zeolite and NC composite. In spectrum of NC composite (b), a peak at 2370 cm^{-1} appears which is associated to hydroxyl groups (-OH) stretch from strongly H-bonded-COOH.³⁷ Also the band at 2370 cm^{-1} can be probably due to C=O stretching induced by carboxylation of the carbon nanotubes.³⁸ In addition, peaks at $2850\text{-}2960\text{ cm}^{-1}$ indicate the presence of $\text{CH}_2\text{CH}_2\text{CH}_2\text{-NH}_2$ groups due to grafting of APTES on MWCNTs surface. These peaks confirm the incorporation of amine modified MWCNTs into the zeolite structure. Furthermore, these spectra show that MWCNTs incorporation did not destroy the zeolite crystal structure.

Figure 3

The SEM images of NaY zeolite and NC composite are shown in Fig. 4. As can be seen, after MWCNT incorporation, the crystalline shape of NaY zeolite in the composite has not changed. The morphologies of NC composites display that the MWCNTs are well blended with NaY zeolite. It can be seen that the size of NaY zeolite crystals in the NC composite is smaller than those in the pure NaY zeolite. It is because of the increase of nucleation sites for the formation of NaY zeolite crystals by MWCNTs, leading to the smaller size of NaY zeolite crystals.

Figure 4

Nitrogen adsorption–desorption isotherms of NaY zeolite and NC composite at 77 K (Fig. 5) are of a typical type I isotherm, which indicate the microporous feature of these composites. The pore characteristics of adsorbents are listed in Table 1. The results show that when MWCNTs incorporate into NaY zeolite, the surface area and micropore volume of NC composite improve, due to the formation of extra micropores. Furthermore, the crystal size reduction may also contribute to the increase of the surface area of NC composite. The effect of particle size on the surface area of adsorbents has also been reported by others.^{39,40}

Figure 5

Table 1

Adsorption Measurement

The pure CO₂, CH₄ and N₂ adsorption isotherms on NaY zeolite and NC composite at 298 K were investigated and are shown in Figs. 6 and 7, respectively. Table 2 shows the CO₂, CH₄ and N₂ adsorption capacities of MWCNTs, NaY zeolite and NC composite at 298 K and 348 K and P = 1 bar.

Figure 6

Figure 7

Table 2

As expected, adsorption capacity of the three gases enhanced after incorporation of MWCNTs because of the increase in the BET surface area and micropore volume of the NC composite. However, as seen in Figs. 6 and 7, the NC composite presented a significant increase in the adsorption capacity of CO₂ in comparison with CH₄ and N₂ that could be due to the reaction between the surface amine groups with the CO₂ molecules and also because of the high quadrupole moment of CO₂ molecules.

Fig. 8 shows the effect of temperature on CO₂ and N₂ adsorption capacity on NC composite. The adsorption capacity of the both gases decreases with the increasing temperature. The decrease of adsorption capacity with rising temperature implies that adsorption process is exothermic and physisorption.

Figure 8

Three of the most common adsorption models, the Freundlich,⁴¹ Langmuir,⁴² and Sips⁴³ isotherms, were used to correlate the experimental data of CO₂ and CH₄ adsorption on NaY zeolite and NC composite. The values of model parameters are given in Table 3. Langmuir isotherm corresponds to homogeneous adsorbent surfaces and Freundlich isotherm refers to multilayer adsorption on heterogeneous surfaces.⁴⁴ Langmuir isotherm is represented by the following equation:

$$q = q_m \frac{bP}{(1+bP)} \quad (1)$$

Where q is the adsorbed capacity (mmol g⁻¹) at equilibrium pressure P, q_m and b (KPa⁻¹) are the maximum amount of gas adsorbed (mmol g⁻¹) and the Langmuir constant, respectively.

Freundlich isotherm equation is given as follows:

$$q = K_f P^{1/n} \quad (2)$$

Where n and k_f (mmol g⁻¹ KPa^{1/n}) are the Freundlich constants related to the intensity of adsorption and the adsorption capacity, respectively.

The Sips isotherm is the combined formula of Langmuir and Freundlich equations which is given by Eq.(3):

$$q = q_m \frac{(bP)^{1/n}}{1+(bP)^{1/n}} \quad (3)$$

Where q (mmol g⁻¹) is the amount of gas adsorbed at equilibrium pressure of P (KPa), q_m is the maximum adsorption capacity, b (KPa⁻¹) is the adsorption equilibrium constant which shows the adsorbate affinity for the surface of adsorbent, and n is the heterogeneity parameter.⁴⁵

The fitting accuracy of the proposed model for the experimental data was estimated by an error function based on the average percent deviation calculated according to:

$$ARE\% = \frac{100}{N} \sum_{i=1}^N \left| \frac{q_i^{exp} - q_i^{cal}}{q_i^{exp}} \right| \quad (4)$$

Where ARE (%) is the average percent deviation, N is the number of data points available in the adsorption equilibrium isotherms, and q^{exp} and q^{cal} are the experimental and calculated amounts adsorbed (mmol/g), respectively.

As shown in Table 3, among the three isotherms mentioned above, the Sips isotherm with high correlation coefficients ($R^2 > 0.99$) and an average percent deviation value of less than 2% provides the best model for adsorbents, and presents the excellent agreement between the model parameters and the experimental data, which indicated the heterogeneous nature of the adsorbents surface.

Table 3

Adsorption Selectivity for gases

The pure component selectivity for gases was obtained from their adsorption isotherms. By applying Eq (5),⁴⁶ the adsorption selectivity of gas 1 over gas 2 can be calculated, where V_1 and V_2 are the volumes of gases 1 and 2 adsorbed at certain temperature and pressure, respectively.

$$A_{1/2} = \frac{V_1}{V_2}, T, P \quad (5)$$

Fig. 9 shows the adsorption selectivities of CO₂/CH₄ on NaY zeolite, CNT and NC composite at different pressures and 298 K. As is clear, the NC composite has higher selectivity than NaY zeolite. Incorporation of CNTs has significantly improved the selectivity of the NC composite compared with NaY zeolite. The formation of the NC composite by NaY zeolite crystal growth on CNTs surface significantly increases the micropore volume compared with NaY zeolite and also creates polarized activated sites or special structures.^{31,35} Consequently, CO₂ molecules with the high quadrupole moment have a greater tendency towards NC composite and therefore, the selectivity of NC composite is higher than NaY zeolite.

Figure 9

Table 4 shows selectivities of CO₂ over CH₄ obtained in this study in comparison to other values found in the literature. The selectivity of NC composite is higher than that of other porous materials (except Cu₃(BTC)₂) under similar conditions.

Table 4

Because of high hydrothermal stability and more cost-effectiveness of zeolites compared to other porous materials such as metal organic frameworks, NC composite is a promising candidate for separation and purification of CO₂ from CO₂/CH₄ mixtures by selective adsorption.

For reduction of greenhouse gas emissions, the removal of CO₂ from flue gas in post combustion process is important. The adsorption selectivities of CO₂/N₂ on NaY zeolite and NC composite at two different temperatures and P < 5 bar are shown in Fig. 10. The NC composite has higher selectivity than NaY zeolite. Moreover, selectivities of CO₂/N₂ significantly increase at high temperature and low pressure. Since the flue gas pressure, as well as its CO₂ concentration is low, therefore, NC composite is a promising candidate for the capture of CO₂ from flue gas. Rising temperature has enhanced selectivity of CO₂/N₂ on NC composite.

Figure 10

Conclusions

Zeolite/carbon nanotube composite has been successfully synthesized with hydrothermal method and characterized. The surface area and pore volume of the NC composite and consequently its enhanced adsorption are attributed to increase of nucleation sites after incorporation of MWCNTs into zeolite. Selectivity of NC composite for CO₂/CH₄ mixture (2.22) at 298 K and p = 1 bar was higher than that of NaY zeolite (1.36). Because CO₂ molecules have high quadrupole moment while CH₄ molecules do not have a quadrupole moment. Selectivities of NC composite for CO₂/N₂ mixture at p = 1 bar and 298 K and 348 K are 15.2 and 18.9, respectively, are higher than those of NaY zeolite (8.8 and 13.9 at 298 K and 348 K, respectively). Due to the obtained results in this study, NC composite can be a suitable material for the separation and purification of gases in the industrial applications.

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271 **References**

- 272 (1) Abdesshahian, P.; Dashti, M.; Kalil, M.; Yusoff, W. *Biotechnology* **2010**, *9*, 274.
273 (2) Cavenati, S.; Grande, C. A.; Rodrigues, A. E. *Journal of Chemical & Engineering Data* **2004**, *49*, 1095.
274 (3) Bucior, B. J.; Chen, D.-L.; Liu, J.; Johnson, J. K. *The Journal of Physical Chemistry C* **2012**, *116*, 25904.
275 (4) Peng, X.; Wang, W.; Xue, R.; Shen, Z. *AIChE Journal* **2006**, *52*, 994.
276 (5) Auta, M.; Hameed, B. H. *Chemical Engineering Journal* **2014**, *253*, 350.
277 (6) Luebke, D.; Myers, C.; Pennline, H. *Energy & Fuels* **2006**, *20*, 1906.
278 (7) Xiang, Z.; Cao, D.; Lan, J.; Wang, W.; Broom, D. P. *Energy & Environmental Science* **2010**, *3*, 1469.
279 (8) Salles, F.; Jobic, H.; Devic, T.; Guillermin, V.; Serre, C.; Koza, M. M.; Ferey, G.; Maurin, G. *The Journal*
280 *of Physical Chemistry C* **2013**, *117*, 11275.
281 (9) Palomino, M.; Corma, A.; Jorda, J. L.; Rey, F.; Valencia, S. *Chemical Communications* **2012**, *48*, 215.
282 (10) Li, P.; Handan Tezel, F. *Microporous and Mesoporous Materials* **2007**, *98*, 94.
283 (11) Xu, X.; Zhao, X.; Sun, L.; Liu, X. *Journal of Natural Gas Chemistry* **2009**, *18*, 167.
284 (12) Montanari, T.; Finocchio, E.; Salvatore, E.; Garuti, G.; Giordano, A.; Pistarino, C.; Busca, G. *Energy*
285 **2011**, *36*, 314.
286 (13) Xu, X.; Zhao, X.; Sun, L.; Liu, X. *Journal of Natural Gas Chemistry* **2008**, *17*, 391.
287 (14) McEwen, J.; Hayman, J.-D.; Ozgur Yazaydin, A. *Chemical Physics* **2013**, *412*, 72.
288 (15) Li, Y.; Yi, H.; Tang, X.; Li, F.; Yuan, Q. *Chemical Engineering Journal* **2013**, *229*, 50.
289 (16) Dantas, T. L. P.; Luna, F. M. T.; Silva Jr, I. J.; Torres, A. E. B.; de Azevedo, D. C. S.; Rodrigues, A. E.;
290 Moreira, R. F. P. M. *Chemical Engineering Journal* **2011**, *172*, 698.
291 (17) Mulgundmath, V. P.; Tezel, F. H.; Saatcioglu, T.; Golden, T. C. *The Canadian Journal of Chemical*
292 *Engineering* **2012**, *90*, 730.
293 (18) Bezerra, D.; Oliveira, R.; Vieira, R.; Cavalcante, C., Jr.; Azevedo, D. S. *Adsorption* **2011**, *17*, 235.
294 (19) Chatti, R.; Bansawal, A. K.; Thote, J. A.; Kumar, V.; Jadhav, P.; Lokhande, S. K.; Biniwale, R. B.;
295 Labhsetwar, N. K.; Rayalu, S. S. *Microporous and Mesoporous Materials* **2009**, *121*, 84.

- 296 (20) Chen, X.; Guo, J.; Fu, Z.; He, H.; Long, Y. *Journal of Porous Materials* **2013**, *20*, 1271.
- 297 (21) Lopes, F. V. S.; Grande, C. A.; Ribeiro, A. M.; Vilar, V. J. P.; Loureiro, J. M.; Rodrigues, A. E. *Journal*
298 *of Chemical & Engineering Data* **2010**, *55*, 184.
- 299 (22) Zhao, Z.; Cui, X.; Ma, J.; Li, R. *International Journal of Greenhouse Gas Control* **2007**, *1*, 355.
- 300 (23) Katsuki, H.; Furuta, S.; Watari, T.; Komarneni, S. *Microporous and Mesoporous Materials* **2005**, *86*,
301 145.
- 302 (24) Ma, J.; Sun, H.; Su, S.; Cheng, W.; Li, R. *Journal of Porous Materials* **2008**, *15*, 289.
- 303 (25) Ma, J.; Tan, J.; Du, X.; Li, R. *Microporous and Mesoporous Materials* **2010**, *132*, 458.
- 304 (26) Okada, K.; Shimizu, Y.-I.; Kameshima, Y.; Nakajima, A. *Journal of Porous Materials* **2005**, *12*, 281.
- 305 (27) Lee, J.-S.; Kim, J.-H.; Kim, J.-T.; Suh, J.-K.; Lee, J.-M.; Lee, C.-H. *Journal of Chemical & Engineering*
306 *Data* **2002**, *47*, 1237.
- 307 (28) Kim, J.-H.; Lee, C.-H.; Kim, W.-S.; Lee, J.-S.; Kim, J.-T.; Suh, J.-K.; Lee, J.-M. *Journal of Chemical &*
308 *Engineering Data* **2003**, *48*, 137.
- 309 (29) Adinata, D.; Daud, W.; Aroua, M. *Journal of Nanoparticle Research* **2007**, *9*, 555.
- 310 (30) Jin, M.; Kurniawan, W.; Hinode, H. *Journal of chemical engineering of Japan* **2006**, *39*, 154.
- 311 (31) Xiang, Z.; Peng, X.; Cheng, X.; Li, X.; Cao, D. *The Journal of Physical Chemistry C* **2011**, *115*, 19864.
- 312 (32) Yang, Y.; Ge, L.; Rudolph, V.; Zhu, Z. *Dalton Transactions* **2014**, *43*, 7028.
- 313 (33) Anbia, M.; Hoseini, V. *Chemical Engineering Journal* **2012**, *191*, 326.
- 314 (34) Xiang, Z.; Hu, Z.; Cao, D.; Yang, W.; Lu, J.; Han, B.; Wang, W. *Angewandte Chemie International*
315 *Edition* **2011**, *50*, 491.
- 316 (35) Dumeé, L.; He, L.; Hill, M.; Zhu, B.; Duke, M.; Schutz, J.; She, F.; Wang, H.; Gray, S.; Hodgson, P.;
317 Kong, L. *Journal of Materials Chemistry A* **2013**, *1*, 9208.
- 318 (36) Pourebrahimi, S.; Kazemeini, M.; Ganji Babakhani, E.; Taheri, A. *Microporous and Mesoporous*
319 *Materials* **2015**, *218*, 144.
- 320 (37) Su, F.; Lu, C.; Cnen, W.; Bai, H.; Hwang, J.F. *Science of the Total Environment* **2009**, *407*, 3017.
- 321 (38) https://gcep.stanford.edu/pdfs/PE5v0Xtftasff29ZflqL4Q/3.6_Wilcox_Public_Version_2012.pdf.
- 322 (39) Liu, Q.; Jin, L.-N.; Sun, W.-Y. *Chemical Communications* **2012**, *48*, 8814.
- 323 (40) Ge, L.; Zhou, W.; Rudolph, V.; Zhu, Z. *Journal of Materials Chemistry A* **2013**, *1*, 6350.
- 324 (41) Okeola, F.; Odebunmi, E. *Advances in Environmental Biology* **2010**, 329.

- 325 (42) Garnier, C.; Finqueneisel, G.; Zimny, T.; Pokryszka, Z.; Lafortune, S.; Défossez, P.; Gaucher, E. C.
326 *International Journal of Coal Geology* **2011**, 87, 80.
- 327 (43) Foo, K.; Hameed, B. *Chemical Engineering Journal* **2010**, 156, 2.
- 328 (44) Rao, G. P. C.; Satyaveni, S.; Ramesh, A.; Sessaiah, K.; Murthy, K.; Choudary, N. *Journal of*
329 *environmental management* **2006**, 81, 265.
- 330 (45) Do, D. D. *Adsorption Analysis: Equilibria and Kinetics*; World Scientific, **1998**; Vol. 2.
- 331 (46) Pawar, R. R.; Patel, H. A.; Sethia, G.; Bajaj, H. C. *Applied Clay Science* **2009**, 46, 109.
- 332 (47) Xiang, Z. H.; Lan, J. H.; Cao, D. P.; Shao, X. H.; Wang, W. C.; Broom, D. P. *The Journal of Physical*
333 *Chemistry C* **2009**, 113, 15106.
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354 **Table captions:**

355 **Table 1.** Structural properties of NaY zeolite and NC composite

356 **Table 2.** Gas adsorption capacities of NaY zeolite, CNT and NC composite at two temperatures and 1 bar.

357 **Table 3.** Langmuir, Freundlich, and Sips isotherm parameters for the adsorption of CO₂ and CH₄ on NaY
358 zeolite and NC composite

359 **Table 4.** Selectivities of CO₂ over CH₄ in different porous materials at 298K and 1 bar

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Figure captions:

Fig. 1 Schematic diagram of volumetric system for adsorption test.

Fig. 2 XRD patterns of the NaY zeolite and NC composite.

Fig. 3 FT-IR spectra of NaY zeolite and NC composite.

Fig. 4 SEM images of NaY zeolite (a,b) and NC composite (c,d).

Fig. 5 N₂ adsorption – desorption isotherms of NaY zeolite and NC composite at 77 K.

Fig. 6 Adsorption isotherms of CO₂ on NaY zeolite and NC composite at 298 K.

Fig. 7 Adsorption isotherms of CH₄ and N₂ on NaY zeolite and NC composite at 298 K.

Fig. 8 Adsorption isotherms of CO₂ on NC composite at 298 K and 348 K.

Fig. 9 Selectivities of CO₂ over CH₄ in NaY zeolite, CNT and NC composite at 298 K.

Fig. 10 Selectivities of CO₂ over N₂ in NaY zeolite and NC composite at 298 K and 348 K.

Table 1 Structural properties of NaY zeolite and NC composite

Adsorbent	S_{BET} (m ² /g)	Pore volume (cm ³ /g)
MWCNT	> 200	—
NaY zeolite	212	0.213
NC	407.49	0.349

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Table 2 Gas adsorption capacities of NaY zeolite, CNT and NC composite at two temperatures and 1 bar.

Adsorbent	Gas adsorption capacity (mmol/g)					
	298 K			348 K		
	CO ₂	CH ₄	N ₂	CO ₂	CH ₄	N ₂
CNT	1.19	0.63	0.17	1.02	—	0.09
NaY	1.9	1.4	0.21	1.67	—	0.12
NC	4.1	1.86	0.27	3.6	—	0.19

Table 3 Langmuir, Freundlich, and Sips isotherm parameters for the adsorption of CO₂ and CH₄ on NaY zeolite and NC composite

Adsorbent	CO ₂		CH ₄	
	NaY	NC	NaY	NC
Sips				
q _m (mmol/g)	1.88	4.1	1.39	1.93
b(KPa ⁻¹)	0.036	0.067	0.034	0.04
n	0.262	0.397	0.352	0.426
R ²	0.995	0.999	0.996	0.998
ARE%	1.05	0.73	0.71	1.61
Langmuir				
q _m (mmol/g)	2.07	4.24	1.50	2.14
b(KPa ⁻¹)	0.039	0.199	0.036	0.056
R ²	0.932	0.984	0.945	0.947
ARE%	4.73	2.66	4.28	4.83
Freundlich				
K _f	0.685	3.17	0.686	0.643
n	5.7	21.39	8.08	5.22
R ²	0.830	0.964	0.874	0.854

Table 4 Selectivities of CO₂ over CH₄ in different porous materials at 298K and 1 bar

Adsorbent	CO ₂ /CH ₄ selectivity	References
CNT	1.88	This study
NaY	1.36	This study
NC	2.22	This study
MOF-177	0.89	31
ZIF-8	1.32	31
Cu ₃ (BTC) ₂	2.28	34
UMCM-1	1.82	47

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Fig. 1 Schematic diagram of volumetric system for adsorption test.

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Fig. 2 XRD patterns of the NaY zeolite and NC composite.

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Fig. 3 FT-IR spectra of NaY zeolite and NC composite.

Fig. 4 SEM images of NaY zeolite (a,b) and NC composite (c,d).

Fig. 5 N₂ adsorption–desorption isotherms of NaY zeolite and NC composite at 77 K.

Fig. 6 Adsorption isotherms of CO₂ on NaY zeolite and NC composite at 298 K.

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Fig. 7 Adsorption isotherms of CH_4 and N_2 on NaY zeolite and NC composite at 298 K.

Fig. 8 Adsorption isotherms of CO₂ on NC composite at 298 K and 348 K.

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Fig. 9 Selectivities of CO₂ over CH₄ in NaY zeolite, CNT and NC composite at 298 K.

Fig. 10 Selectivities of CO₂ over N₂ in NaY zeolite and NC composite at 298 K and 348 K.

623 Graphical Abstract

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638 **Highlights**

- 639 • NaY/CNT composite was synthesized by the hydrothermal method and characterized.
- 640 • The incorporation of MWCNT improved the porosity of the zeolite.
- 641 • CO₂, CH₄ and N₂ adsorption capacity enhanced after incorporation of MWCNTs into the zeolite.
- 642 • NC composite showed improved selectivity for CO₂/CH₄ and CO₂/N₂.
- 643 • Effect of temperature on CO₂ selectivity over N₂ was studied.

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