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Effects of acidification time of MWCNTs† on carbon dioxide capture of liquid-like MWCNTs organic hybrid materials

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In this paper, liquid-like MWCNTs nanoparticles organic hybrid materials (MWCNTs-NOHMs) without solvent at room temperature (25°C) were prepared by employing MWCNTs with different acidification time as core, KH560 as corona and M2070 as canopy. The acidification time of MWCNTs on CO_2 capture capacity of MWCNTs-NOHMs were investigated. The number of amine groups on the surface of MWCNTs-NOHMs increased with the prolongation of acidification time. The CO_2 capture capacity of MWCNTs-NOHMs decreased with extend of acidification time of MWCNTs. This is owe to the superior fluidity, poorer viscosity of shorter acid MWCNTs-NOHM. It providedlargermolecule interval and weaker intermolecular forces and made it easier for CO_2 to charge into the potential space. CO_2 can react withamine groups. However, because of the low fluidity and the high viscosity of longer acid MWCNTs-NOHM, its physisorption was unsatisfactory. Chemisorption was also influenced via reducing the contact between CO_2 and reactive groups. The regeneration capacity and adsorption stability of MWCNTs-NOHMs are great, rendering them very potential materialsin CO_2 adsorption.

Introduction

According to the report of the UN Intergovernmental Panel on Climate Change (IPCC), the content of CO_2 is relatively stable until the 18th century. However, rising velocity has increased dramatically since the mid-20th century. It is estimated that CO_2 concentration in the atmosphere will increase doubled than before industrialization in 21 century.[1-3] CO_2 is the main greenhouse gas. It is very significant and demanding to pay immediate attention to the capture and storage of CO_2.

Alkanolamine is considered as mainly common chemical adsorption material.[4-10] It has high capture capacity, but its adsorption performance can not meet the actual demand. This is because of the corrosion on the reactor, the loss of alkanolamine during reaction due to its high volatility, the high cost of regeneration. Therefore, it is imperative to research the new adsorbent material.[11-16] Organic/inorganic nanocomposite system with both performance of nanoparticles and polymers, has potential applications in material aspects of CO_2 capture.

The liquid-like NOHMs were prepared by ionic[17-19] or covalent bonds[20] . The inorganic nanoparticles were grafted with oligomers. Compared with alkanolamine, there are several advantages of liquid-like nanoparticles organic hybrid materials.[21-27] For instance, noncorrosiveness, zero vapour pressure, fluidity and structural controllability. As a result of structural controllability, the groups, which can capture CO_2 like amine oligomer, were grafted on the surface of nanoparticles.

Several works[28, 29] have been reported in the field of liquid-like NOHMs for capturing CO_2. Kun-Yi Andrew Lin and co-workers researched about effects of bonding types and functional groups of liquid-like NOHMs on CO_2 capture, as well as the effect of other gas like SO_2 on CO_2 capture. They found that the capture capacity of liquid-like NOHMs synthesized by covalent bonds was superior. SO_2 changed the CO_2 capture behaviours in liquid-like materials. Howerer, the effect of nanoparticles on CO_2 capture was not mentioned.

Previous studies[11, 30] showed that amine-modified MWCNTs had a certain CO_2 capture capacity and recyclability. This is because MWCNTs have a hollow structure. However, the modified MWCNTs remained solid state at room temperature and aggregated easily. This led to reduction in the contact surface of MWCNTs with CO_2. Therefore, the CO_2 capture capacity was reduced. Our team had reported the effect of canopy structures on CO_2 capture capacity of MWCNTs-NOHM employing modified MWCNTs as core.[31, 32] The aggregate problem of MWCNTs was solved. At the same time the MWCNTs-NOHM may have a stronger effect in terms of CO_2 capture capacity. The core MWCNT itself had physical capture capacity while the amine groups had chemical capture capacity. The entropy effect also played a role in CO_2 capture capacity.

As core in the MWCNTs-NOHM, acidification of MWCNTs is necessary. The size of cores and surface properties of

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† Abbreviations: MWCNTs, multi-walled carbon nanotubes.

MWCNTs will be changed after acidification. The group content on the surface of acid MWCNTs affect the percentage of corona and canopy in the MWCNTs-NOHM and the content of amine groups, which affects the CO_2 capture capacity of MWCNTs-NOHM. In addition, the content of organic chains affect the potential capture space and the active sites of MWCNTs-NOHM. It also greatly affects the CO_2 capture capacity of MWCNTs-NOHM.

In this paper, liquid-like MWCNTs-NOHM with different acidification time of MWCNTs acted as core had been synthesized. The effect of different size and performance of MWCNTs on CO_2 capture capacity had been studied.

Experimental

Materials and synthetic procedures

MWCNTs of 20–30 nm diameter and 5-15 um length were provided by Chengdu organic chemicals Co., Ltd. (3-Glycidyloxypropyl) trimethoxysilane (KH560, 98 wt.%) was from Chengdu aikeda chemicals Co., Ltd. Polyetheramine-M2070 (Mw ~ 2000) was used as polymeric canopy in this study and obtained from Dalian lianhao Co., Ltd. Other analytical grade chemicals were H_2SO_4, HNO_3 and methanol.

MWCNTs were modified with mixed acids (H_2SO_4/ HNO_3, volume ratio 3:1) at 70°C. The acidification times were 3h, 5h and 7h, respectively. The long organic chains grafted on the surface of MWCNTs as solvent in NOHMs. If the acidification time is not long enough, the –OH and–COOH groups on the surface of MWCNTs are insufficient, leading the number of grafted long organic chains decreased. Thus the NOHMs can not flow like liquid without solvent. Our team had synthesized many MWCNTs-NOHMs with different acidification time of MWCNTs. We found that 3h is the limit of shortest acidification time. For remove residual acid, the products were washed with the deionized water and dried at 70 °C for 24h. Then 5 mmolKH560 was added to the diluted solution of Polyetheramine-M2070 (15wt.%, diluted with methanol and deionized water) dropwise. The molar ratio of KH560 and M2070 was 1 to 1. The mixed solution was stirred for 12h at 45°C. Next, 0.5 g acid MWCNTs were mixed with methanol through the ultrasound dispersion for 30mins, and then added to the mixed solution. The mixture was reacted at 25°C for 5h under mechanicalstirring to ensure complete reaction. The excess M2070 was removed in the dialysis tubing (3500 MWCO, Xi'an luosenbo biotech Co., Ltd) for 12h. At last, the liquid-like MWCNTs-NOHMs were obtained after dried at 35 °C in vacuum oven to remove ~~methanol~~solvent.

In this study, three specific liquid-like MWCNTs-NOHMs were prepared and named as MWCNTs-NOHM-3h, MWCNTs-NOHM-5h and MWCNTs-NOHM-7h, respectively. It denoted the acidification time of MWCNTs in the liquid-like MWCNTs-NOHMs.

Characterization

Thermo gravimetric analysis (TGA) measurements were taken under N_2 flowing with heating rate of 10°C /min from 25°C to 600°C by using TGA Q50 TA instrument. A Brookfield R/S plus Rotational Rheometer was used to measure the viscosity of NOHMs with shearing rate of $50s^{-1}$ for 5mins at 25°C. The temperature was stabilized by using a TC-650 constant temperature water bath. Fourier Transform infrared spectra (FTIR) were shown by a WQF-310 FTIR spectrometer and ranged from 400-4000 cm^{-1} at room temperature. The samples were measured with KBr pellet. Transmission electron microscope (TEM) images of acid MWCNTs and MWCNTs-NOHM were taken to study the internal morphology of samples. A JEM-2100 instrument was used at an accelerating voltage of 100 kV after a few drops of sample/ethanol solution were placed on a copper grid and dried. X-ray Photoelectron Spectroscopy （XPS, Kratos Axis Ultra DLD）was used to measure the contents of elements and groups of simples. The curves were obtained after a few samples were placed on a conductive blanket. The wide scan ranged from 0eV to 760eV.

Capture CO_2 measurements were tested with a home-made capture instrument[28] (Figure.1). The instrument was made up with a CO_2 cylinder, a pressure transducer (Chengdu lankehedun automation equipment Co., Ltd, CX-206), a press chamber of 30mL volume(recorded as V), an electronic analytical balance (Shanghai yoko instrument Co., Ltd, FA-2004B), a vacuum pump (Wenling suli electromechanical Co., Ltd, 2XZ-4), a few high pressure stainless steel hoses and ball valves. To begin with, the weight of sample was measured by an electronic analytical balance and the reading was recorded as m (g). Next, the MWCNTs-NOHM was put into the press chamber. Before each capture test, any air or gas in the press chamber was removed by vacuum pump. Then CO_2 was introduced into the press chamber. The reading of the pressure transducer was recorded as P1 (MPa) simultaneously. After 30mins, the reading of the pressure transducer was recorded as P2 (MPa). P1 and P2 are both CO_2 pressure. The capture capacity C (mmol/g^{-1}) was calculated by equation 1 as follows:

$$\mathrm{C} = \mathrm{V}(P1 - P2) \times 10^3 / mRT \qquad (1)$$

Where R is 8.314(Pa. m^3/mol.K) and T is 298K.

The desorption process lasted for 10 mins by the vacuum pump. Physisorption was removed and chemisorption remained in this process. Firstly, the sample was exposed to the vacuum environment for 10 mins in case of any gas. Then the initial mass of material was tested by an electronic analytical balance (XS104, METTLER TOLEDO) and was recorded as m (g). After sorption CO_2 for 30 mins and desorption for 10 mins, the mass of material was recorded as m1 (g). Thus the CO_2 chemisorption of material Cc (mmol/g-1) was obtained by equation 2 as follows:

$$\mathrm{C}_c = (m1 - m) \times 10^3 / 44m1 \qquad (2)$$

Then the CO_2physisorption of material Cp (mmol/g-1) could be calculated to be C-Cc. Furthermore, the sorption-desorption cycle was run 10 times to investigate the regeneration of materials.

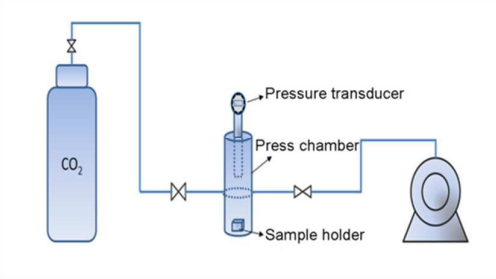

Figure.1.The sketch map of home-made CO_2 capture instrument.

Results and discussion

Characterization of MWCNTs-NOHMs

Figure.2 shows the reaction mechanism of acid MWCNTs with KH560 and M2070. The photo in Figure.2 is MWCNTs-NOHM-3h and shows black viscous flow state at room temperature. This is attributed to the layer of organics, which is consisted of long chains of KH560 and M2070. As a result of this organic layer, the MWCNTs-NOHMs possess both lipophilic and hydrophilic. The three samples were placed on glass slide inclined 30° for 10 mins at room temperature as photographed in Figure.3. From these images we can see that the three samples flowed in the absence of solvents on glass slide and remained black viscous flowing tracks. The track of MWCNTs-NOHM-3h is the longest which shows the best fluidity. MWCNTs-NOHM-5h is the secondary one.

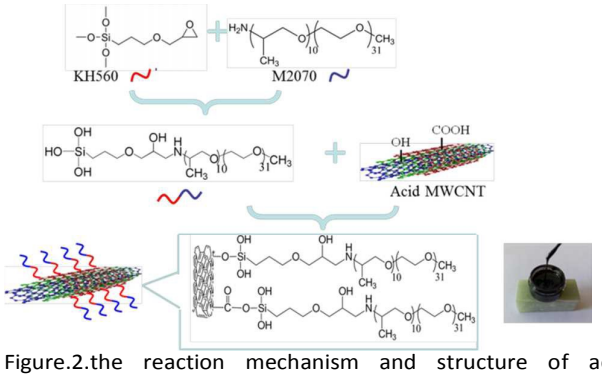

Figure.2.the reaction mechanism and structure of acid MWCNTs with KH560 and M2070

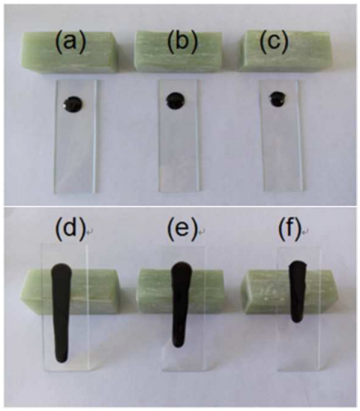

Figure.3. Fluidity photos of MWCNTs-NOHMs inclined 30° for 10 mins at room temperature, (a), (b) and (c) initial state of MWCNTs-NOHM-3h, 5h and 7h. (d), (e) and (f) finial state of MWCNTs-NOHM-3h, 5h and 7h after 10 mins

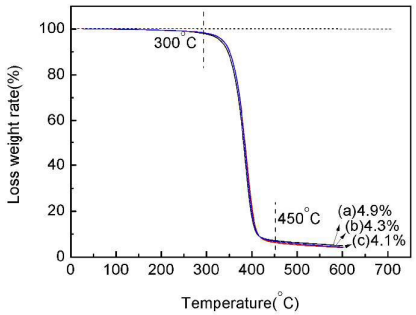

Figure.4. TGA curves of (a) MWCNTs-NOHM-3h, (b) MWCNTs-NOHM-5h, (c) MWCNTs-NOHM-7h.

The TGA curves of NOHMs are shown in Figure.4. The loss weight of NOHMs is few below 300 ℃. It reveals that the NOHMs without solvent still show liquid-like state at room temperature, owing to the flexible long chains of polyetheramine as canopy. Thereby, the NOHMs are stable as CO_2capture sorbents. Moreover, corona and canopy are decomposed above 300 ℃. Nanoparticles are left over above 450℃.It indicates that the contents of core in MWNTs-NOHM-3h, 5h and 7h are up to 4.9wt.%, 4.3wt.% and 4.1wt.%, respectively. Then the content of KH-560 and M-2070inMWNTs-NOHM-3h, 5h and 7h are 95.1 wt.%, 95.7 wt.% and 95.9 wt.% , respectively. The dense surface coverage recorded as *n* is used to represent the number of carbon atoms of per organic chain (KH560 and M2070) grafted on MWCNTs. It is calculated by formula (5).

$$n = \frac{\omega_c}{M_c} / \frac{\omega_o}{M_o} \qquad (5)$$

Where ω_C and ω_O represent the weight fraction of carbon atoms and organism in the system. Mc and Mo are the mole mass of carbon atoms and organism, and are up to 12 g·mol^{-1} and 2236 g·mol^{-1}, respectively. The dense surface coverage of MWCNTs-NOHMs-3h, 5h and 7h are 9.6, 8.3 and 7.9, respectively. It means that every 10 organic chains share 96 carbon atoms in MWCNTs-NOHMs-3h, 83 carbon atoms in MWCNTs-NOHMs-5h and 79 carbon atoms in MWCNTs-NOHMs-7h. It indicates that longer acidification time of MWCNTs make more organic chains, which provide amine groups in MWCNTs-NOHM.

To compare the viscosity of NOHMs, the viscosity curves of MWCNTs-NOHMs at 25 ℃ are shown in Figure.5. The MWCNTs-NOHM-7h presents the highest viscosity of NOHMs, reaching to 11.5 Pa·s. Besides, the viscosity of MWCNTs-NOHM-3h is the lowest, only 9.5 Pa·s. This result is consistent with the photos which are shown in Figure.3. Furthermore, the results of TGA indicate that the smaller value of dense surface coverage *n,* the more organic chains in MWCNTs-NOHMs. This leads to more friction and less space between the chains, and limiting the molecular chains movement. As a result, the viscosity of MWCNTs-

NOHMs is increased. So the dense surface coverage *n* affects the viscosity of MWCNTs-NOHMs. Smaller value of *n* makes lager viscosity of MWCNTs-NOHMs.

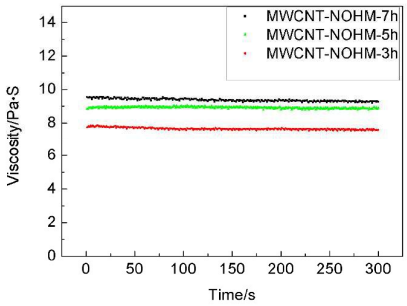

Figure.5. The viscosity curves of MWCNTs-NOHMs at 25 ℃

The FTIR spectra of MWCNTs-NOHMs are illustrated in Figure.6. The spectra of MWCNTs with different acidification time are also included for comparison. When the KH560 is grafted onto the surface of MWCNTs via dehydration-condensation reaction, new absorption band 709 cm^{-1}appears,which is assigned to C-O-Si stretching vibrations in the curves(a), (b) and (c). In these curves, band at 1290cm^{-1} correspond to the secondary amine group -NH- vibrations. This is due to the reaction between epoxy groups of KH560 and -NH_2 of M2070. As expected, the MWCNTs-NOHMs show peaks characteristic of both the KH560 and M2070. The new peaks at 1189cm^{-1}, 1120cm^{-1} and 1471cm^{-1} are assigned to the absorption peak of aliphatic amine, vibrations of ether bond -O- and in-plane bending vibration peak of C-H, respectively. The result of FTIR spectra demonstrates that the MWCNTs-NOHMs were prepared successfully. In order to further demonstrate that the reaction has occurred, FTIR spectra of pristine M2070, intermediate product KH560+M2070 and MWCNTs-NOHMs from 2800-4000 cm^{-1} are shown in Figure.7.Two characteristic absorption peaks of –NH_2near 3290 cm^{-1} and 3360 $cm^{-1}$are observed in the spectra of pristine M2070. The disappearance of these two absorption peaks in the intermediate product KH560+M2070 indicate that KH560 has been successfully grafted to M2070.Furthermore, the –NH_2absorptionpeaks are not observed in MWCNTs-NOHMs. To combine with the absorption peaks in Figure.6 of MWCNTs-NOHMs, the organic layer is grafted to MWCNTs successfully.

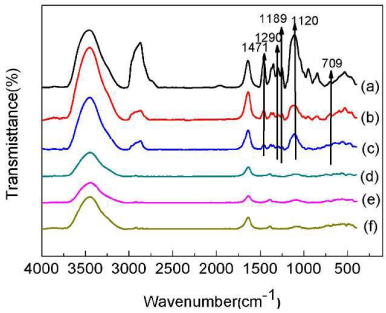

Figure.6. FTIR spectra of acid MWCNTs and MWCNTs-NOHMs, (a) MWCNTs-NOHM-3h, (b) MWCNTs-NOHM-5h, (c) MWCNTs-NOHM-7h,(d) MWCNTs-3h, (e) MWCNTs-5h, (f) MWCNTs-7h

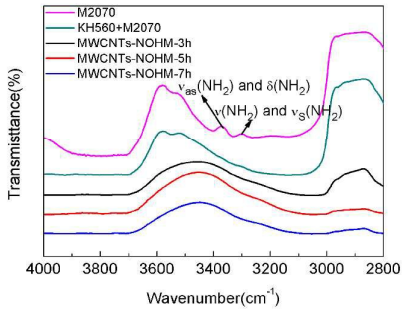

Figure.7. FTIR spectra of pristine M2070, intermediate product KH560+M2070 and MWCNTs-NOHMs.

The TEM images (Figure 8(a), (b) and (c)) show different acidification time of acid MWCNTs. In these images, the length of acid MWCNTs gradually diminished as acidification time become longer. In image (b), the outer wall of acid MWCNTs is decomposed by acids and appears slub. The phenomenon is more obvious in image (c). It is demonstrated that the size of MWCNTs change with the acidification time. The images show that the acid MWCNTs were wrapped with a layer of organics (Figure.8(d), (e), (f)) and reveal that the MWCNTs-NOHM were synthesized successfully, which is consistent with the result of FTIR.

The XPS curves of pristine MWCNTs and acid MWCNTs are shown in Figure.S1, Figure.9 and Figure.S2. The C1s photoelectron is in 284eV and the O1s photoelectron is in 532eV. The wide scan curves of pristine MWCNTs and acid MWCNTs are shown in Figure.S1 (a) and

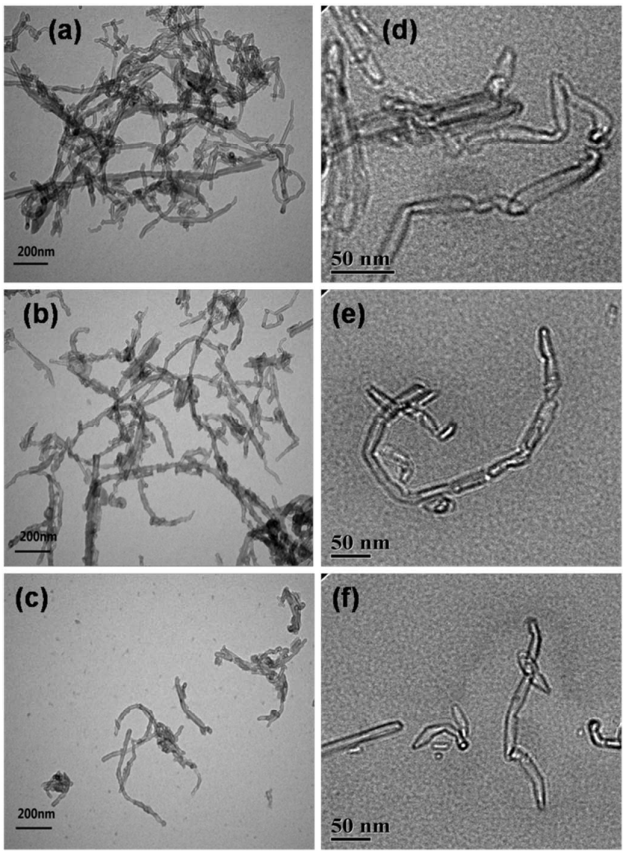

Figure.8 TEM images of different acidification times of acid MWCNTs and MWCNTs-NOHMs. (a) MWCNTs-3h, (b) MWCNTs-5h, (c) MWCNTs-7h, (d) MWCNTs-NOHM-3h, (e) MWCNTs-NOHM-5h, (f) MWCNTs-NOHM-7h.

Figure.S2 (a)-(c), which demonstrate that the oxygen-containing groups are generated on the surface of MWCNTs after acidification. It can be seen clearly that the content of oxygen-containing groups increased with the acidification time of MWCNTs increasing. This is owing to the breaking of MWCNTs during acification. Thereby a large number of oxygen-containing groups like -C-O, C=O and O-C=O are generated.

After a Gaussian curve fitting process, the peak of C1s is divided into four peaks as follows: C-C bond energy in 284.5±0.5eV, -C-O- bond energy in 286.6±0.5eV, -C=O bond energy in 287.8±0.5eV, O-C=O bond energy in 288.9±0.5eV. All of these narrow scan curves are illustrated in Figure.S1 (b) and Figure.9 (a)-(c). After acidification, the content of –COOH increased. Besides, the content of -COOH groups increased as acidification time of acid MWCNTs become longer. From XPS curves of acid MWCNTs, the mass fraction of grafted groups –COOH ($\omega_{\text{-COOH}}$) and –OH ($\omega_{\text{-OH}}$)are gained. They are calculated by the formula (3) and (4) as follow:

$$\omega_{-COOH} = \frac{\omega_{C1S} \times \omega_{-COOH}^{C1S}}{M_C} \times M_{-COOH} \times 100\% \qquad (3)$$

$$\omega_{-OH} = \frac{\omega_{C1S} \times \omega_{-COH}^{C1S}}{M_C} \times M_{-OH} \times 100\% \qquad (4)$$

Where ω_{c1s} presents the weight fraction of C1s in wide scan XPS curves. The mass fraction of C1s in narrow scan XPS curves based on –COOH and –COH are recorded as ω_{-COOH}^{C1S} and ω_{-OH}^{C1S} respectively. M_C, $M_{\text{-COOH}}$ and $M_{\text{-OH}}$ are molar mass. They are 12 g·mol^{-1}, 45 g·mol^{-1} and 17 g·mol^{-1}, respectively. Therefore, according to formula (3) and (4), the $\omega_{\text{-COOH}}$ in NOHM-3h, 5h and 7h are 13.16 wt.%, 24.9 wt.% and 27.76 wt.%, respectively. Moreover, the $\omega_{\text{-OH}}$ in NOHM-3h, 5h and 7h are 33.01 wt.%, 27.87 wt.% and 27.85 wt.%, respectively, because oxidation of -OH yields –COOH. From these evidences we can see that longer acidification time of MWCNTs causing lager total mass fraction of grafted groups in acid MWCNTs.

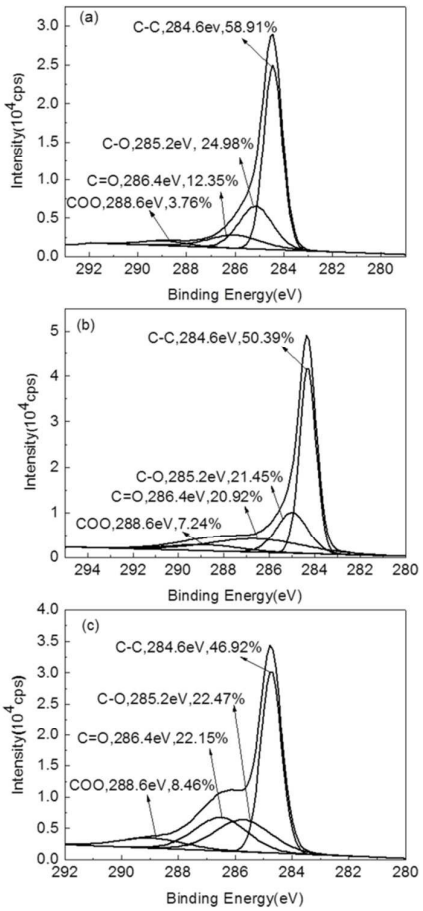

Figure.9. XPS curves of C1s narrow scan of acid MWCNTs, (a) MWCNTs-3h, (b) MWCNTs-5h, (c) MWCNTs-7h

The polymeric corona KH560 can react with -C-OH group and O-C=O group of acid MWCNTs. Therefore, the surface of acid MWCNTs with 7h acidification is grafted with more organic chains and obtains more amine groups from M2070.

The peaks at 400 eV and 100 eV correspond to N1s and Si2p of MWCNTs-NOHM in Figure.S3 (a)-(c). The contents of these two elements are both rised with the increasing of acidification time. It also certificates that MWCNTs-NOHM-7h get more amine groups. The Gaussian curves of C1s of MWCNTs-NOHM

are shown in Figure.10 (a)-(c). The covalent bonds C-N and C-Si formed owing to the reaction shown in Figure.2.

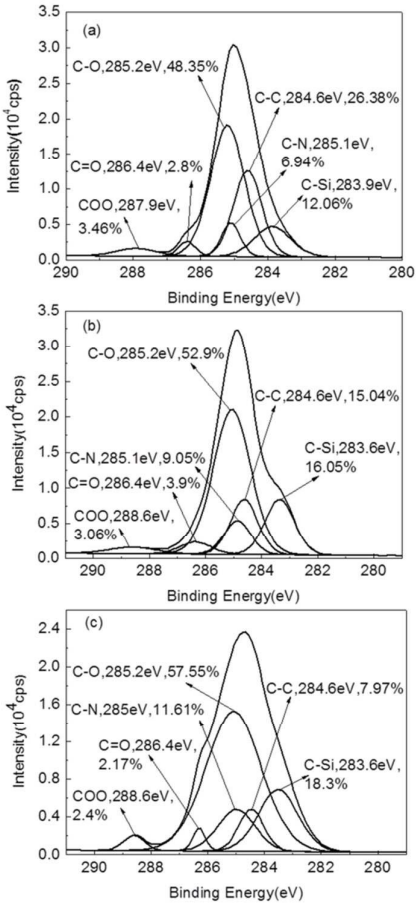

Figure.10. XPS curves of C1s narrow scan of MWCNTs-NOHMs, (a) MWCNTs-NOHM-3h, (b)MWCNTs-NOHM-5h, (c) MWCNTs-NOHM-7h

Study of CO_2capture capacity of MWCNTs-NOHMs

Ping Qu[31] and Peipei Li[32] have reported the effect of canopy structures on CO_2 capture capacity of MWCNTs-NOHM. Not only does the canopy structure, but also the core structure has an important influence on CO_2 capture. In this paper, the effects of different acidification time of MWCNTs as core on CO_2 capture capacity have been studied. CO_2 capture capacity under different CO_2 pressure at room temperature is demonstrated in Figure.11.

It can be seen that the pristine MWCNTs shows lowest adsorption of CO_2 under all CO_2 pressure may be due to its none reactive groups with CO_2 and the hollow structure of MWCNTs can only provide physisorption. The pristine canopy M2070 presents liquid state at room temperature and its CO_2 capture capacity is better than pristine MWCNTs. This is because the primary amine groups of M2070 provide chemisorptions. Besides, physisorption is also exists for M2070.

As shown in Figure.11, the CO_2 capture capacity of three MWCNTs-NOHMs are increased with increasing capture pressure and are all much better than pristine MWCNTs and canopy M2070, and even exceed the summation of them under the same CO_2 pressure. As a result of it, The MWCNTs-NOHMs are proved to be very potential materials in CO_2 adsorption. They are more significant than the previous work reported byK.Y. Andrew Lin and A.H. Alissa Park.[20] They found that CO_2 capture capacity of tPE was slightly better than that of NOHM-I-tPE. It is owing to a portion of amine group was consumed during the synthesis of NOHM-I-tPE. The CO_2 capture capacity of MWCNTs-NOHM

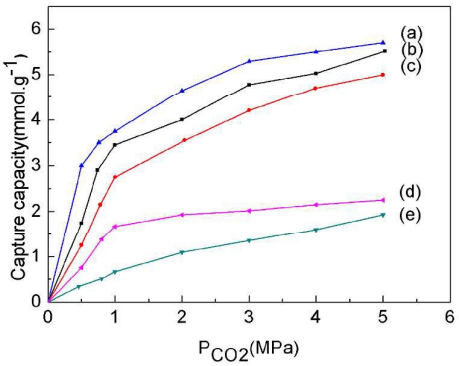

Figure.11.CO_2 capture capacity of (a) MWCNTs-NOHM-3h, (b)MWCNTs-NOHM-5h, (c) MWCNTs-NOHM-7h, (d) M2070, (e) pure MWCNTs under 0-5MPa of CO2 at room temperature.

It is obvious that the CO_2 capture capacity of MWCNTs-NOHMs become well with the shorter acidification time under the same CO_2 pressure. It seems that MWCNTs-NOHM-7h with the most groups has superior CO_2 capture capacity. However, the interesting result is that the CO_2 capture capacity of MWCNTs-NOHM-7h is the worst among the three MWCNTs-NOHMs. This is may be due to the lower fluidity and higher viscosity of MWCNTs-NOHM-7h, reducing the number of amine groups which can react with CO_2. For further investigation of effects on acidification time of MWCNTs on CO_2 capture, the chemisorption and physisorption of MWNTs-NOHMs under different CO_2 pressure at room temperature are shown in Figure.12.

Figure.12 (a) is the chemisorption of pristine MWCNTs, M2070 and three kinds of MWCNTs-NOHMs. It is easily found that the pristine MWCNTs show negligible chemisorption. Its adsorption behaviour is all shown in Figure.12. (b), which shows the physisorption of samples. As shown in Figure.12, the physisorption of pristine M2070 is the minimum. However, its chemisorption is the maximal due to its relatively higher content of primary amine groups in unit mass of M2070.In addition, for these three MWCNTs-NOHMs, the chemisorption of MWCNTs-NOHM-3h is the lowest owing to its low content of secondary amine groups with shorter acidification time of MWCNTs. This result is based on the result of XPS data shown in Figure.10. As the result of XPS test, the content of secondary amine groups of MWCNTs-NOHM-7h is higher than that of MWCNTs-NOHM-5h, but the Figure.12 (a) shows the contrary

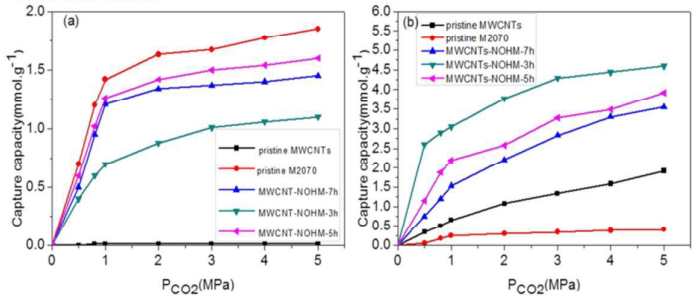

Figure.12 (a) chemisorption CO_2capture capacity of MWCNTs-NOHMs, (b) physisorptionCO_2 capture capacity of MWCNTs-NOHMs under 0-5MPa of CO_2 at room temperature.

result. The chemisorption of MWCNTs-NOHM-7h is little lower than MWCNTs-NOHM-5h. It is because some secondary amine groups are isolated from CO_2 due to the lowest fluidity and the highest viscosity of MWCNTs-NOHM-7h. They reduce the contact between CO_2 and reactive groups. Furthermore, It is clearly seen that physisorption of MWCNTs-NOHMs become lower with the prolongation of acidification time. The physisorption of MWCNTs-NOHMs are mainly based on two ways, namely, hollow structure of MWCNTs and potential space between long chains of corona and canopy. The shorter acid acidification timeMWCNTs-NOHM-3h with superior fluidity and poorer viscosity provide larger molecule interval and weaker intermolecular forces and made it easier for CO_2 to charge into the potential space. Therefore, the CO_2 capture capacity of MWCNTs-NOHM-3h is the best integratedly.

Haipeng Bai[33] reported the NOHM based on POSS, K.Y. Andrew Lin[29] reported the NOHM based on SiO_2 and George Em. Romanos[34] reported the silica nanoparticles encapsulating amine functionalized Ionic Liquids. The CO_2 capture capacity of POSS-NOHM, SiO_2-NOHM and Si-IL is relatively lower than MWCNTs-NOHMs we reported because POSS and SiO_2 nanoparticles have no hollow structure like MWCNTs. The best CO_2 capture capacities of each material are shown and compared in Table.1.

Table.1. CO_2 capture capacities of different adsorbents

adsorbents	MWCNTs-NOHM	POSS-NOHM	SiO_2-NOHM	SiO_2-IL
CO_2 capture capacities/mmol·g^{-1}	5.5	3.8	3.7	3.4

For further study, Figure.13 shows the CO_2 capture data of MWCNTs-NOHMs via 10 times sorption-desorption cycles under 2MPa CO_2 pressure at room temperature. It indicates clearly that there are no efficiency loss and degradation of MWCNTs-NOHMs even via 10 times sorption-desorption cycles.

The regeneration capacity and adsorption stability of MWCNTs-NOHMs are great.

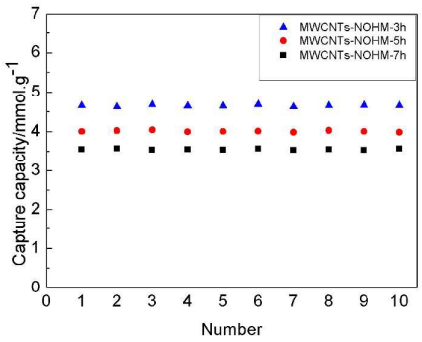

Figure.13. CO_2 capture capacity MWCNTs-NOHMs via 10 sorption-desorption cycles under 2MPa CO_2 pressure at room temperature

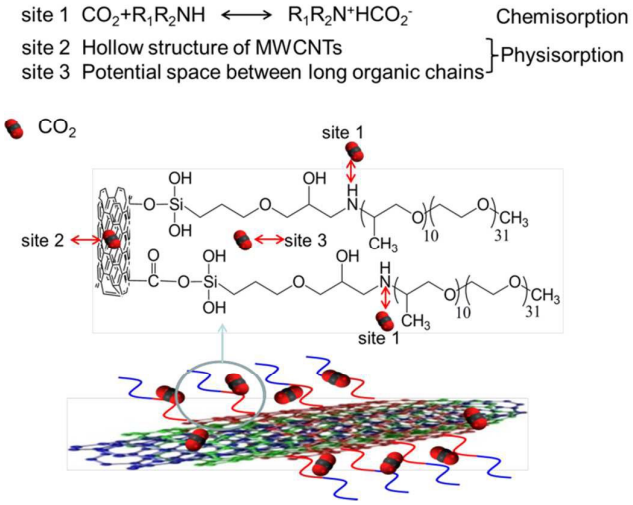

Figure.14. CO_2capturemechanism of MWCNTs-NOHM.

Finally, on the basis of the above results, the CO_2 capturemechanism of MWCNTs-NOHM is illustrated in Figure.14. It can be easily found that more content of –NH- make higher chemisorption. On the contrary, higher viscosity is disadvantageous to both chemisorption and physisorption because it not only reduces the contact between CO_2 and–NH-, but also provides larger molecule interval and weaker intermolecular forces, which make it easier for CO_2 to charge into the potential space. Besides, longer acidification time of MWCNTs make more content of –NH- and higher viscosity of NOHMs. After all, longer acidification time of MWCNTs leads to lower CO_2 adsorption.

Conclusions

Liquid-like MWCNTs organic hybrid materials (MWCNTs-NOHMs) were prepared by employing MWCNTs different acidification time as core, KH560 as corona and M2070 as canopy. It is found that longer acidification time of MWCNTs make more content of amine groups in MWCNTs-NOHMs. In the meantime, the viscosity of MWCNTs-NOHMs increased with longer acidification time. From the test of CO_2 capture capacity, it is concluded that more content of –NH- make

higher chemisorption. On the contrary, higher viscosity is disadvantageous to both chemisorption and physisorption because it not only reduces the contact between CO_2 and–NH-, but also provides larger molecule interval and weaker intermolecular forces, which make it easier for CO_2 to charge into the potential space. Therefore, longer acidification time of MWCNTs causing worse CO_2 capture capacity of MWCNTs-NOHMs. The regeneration capacity and adsorption stability of MWCNTs-NOHMs are great. They are very potential materials in CO_2 adsorption.

Acknowledgements

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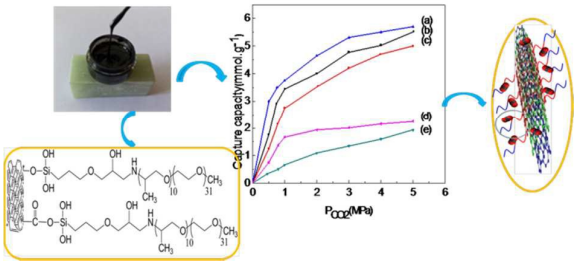
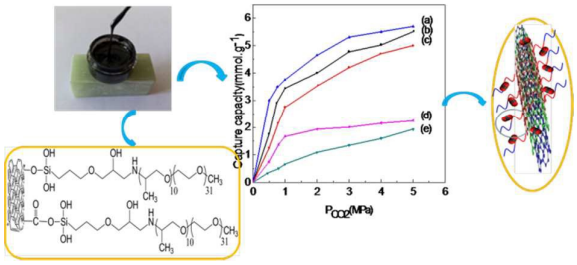


The structure and surface properties of MWCNTs as core in NOHM have a significant influence on CO_2 capture



The structure and surface properties of MWCNTs as core in NOHM have a significant influence on CO_2 capture