

## 1. Sorbents preparation:

### (1) Preparation of pure silica aerogel (PSA)

PSA was prepared by sol-gel method, using TEOS (tetraethylorthosilicate, Sinopharm Chemical Reagent Co., Ltd., AR), H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH (Sinopharm Chemical Reagent Co., Ltd., min. 95%) and HCl with molar ratios of 1.0:3.0:15.6:0.001. The reagents were mixed to hydrolyze TEOS by magnetic stirring in a beaker for 1.5 hours at 50°C. APTES (3-aminopropyltriethoxysilane) (Nanjing Xiangfei Chemistry Research Institute, min. 97%) and C<sub>2</sub>H<sub>5</sub>OH mixture solution (volume ratio: 1:50) was added to adjust pH value to 8.0 for the gelation. TEOS/C<sub>2</sub>H<sub>5</sub>OH (volume ratio: 1:2.5) mixture was added till 6.0 hours after gelatin point and then aged for 6.0 days at 50°C. The wet gel was washed by C<sub>2</sub>H<sub>5</sub>OH solution four times a day. Finally, ethanol supercritical drying was used to dry the wet gel. The drying conditions were set as follows: immerse the wet gel into ethanol solution in a kettle and pre-pressurize to 6.0 Mpa. Raise the temperature gradually up to 265°C and keep the pressure between 10.0~11.0 Mpa. Keep the temperature 265°C and the pressure 10.0 Mpa for 1.5 hours. Release the gas from the kettle gradually and keep the temperature 265°C till the pressure in the kettle equals to the room pressure. Stop heating and clean the sample by pure N<sub>2</sub> gas.

### (2) Preparation of amine modified silica aerogel (AMSA)

The first several steps of AMSA were the same as PSA till aging. Here, aging was named as modification. 6.0 hours after gelation point, APTES diluted with C<sub>2</sub>H<sub>5</sub>OH was added for the modification of wet gel for 6.0 days at 50°C; the molar ratio of APTES to the source material of TEOS was 1:2. C<sub>2</sub>H<sub>5</sub>OH solution was added after modification to replace APTES that remained in the gel network. AMSA was also dried by ethanol supercritical drying like the PSA drying conditions.

The preparation steps are illustrated in Fig. 1:

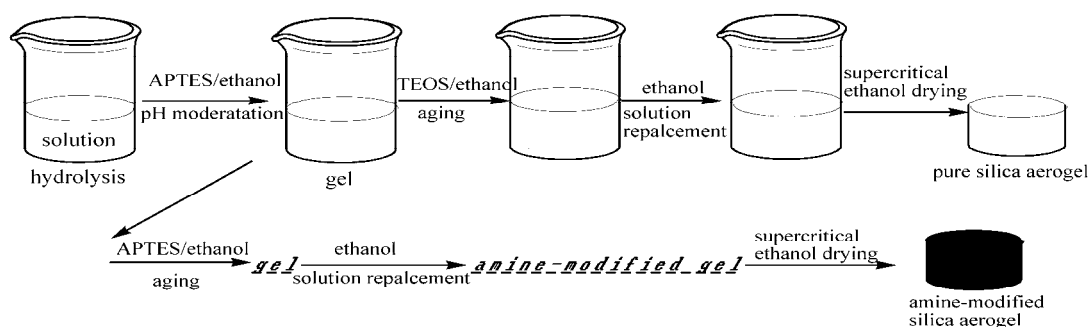
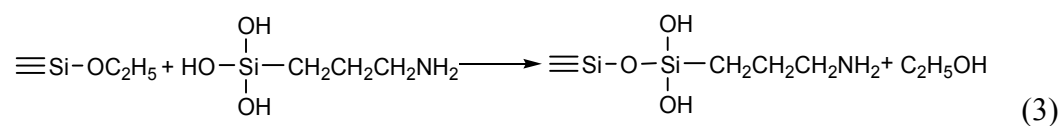
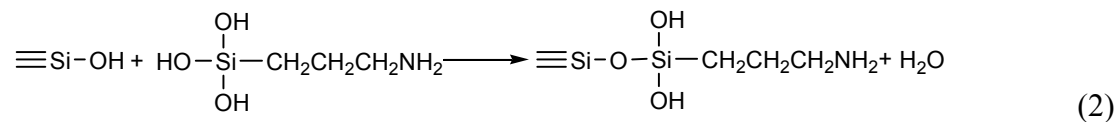
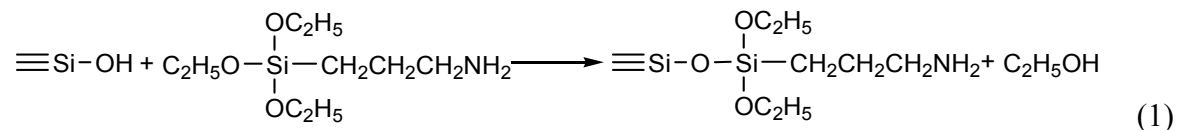


Fig. 1 Preparation of pure and amine-modified silica aerogels

≡Si-OH and ≡Si-OC<sub>2</sub>H<sub>5</sub> on gel surface prepared by TEOS are active to react with APTES or the APTES hydrolyzed production. The modification processes are shown as follows:



## 2. Characterization of sorbents

### (1) Photo of the AMSA without cracks



Fig. 2 A cake of AMSA prepared by ethanol supercritical drying

### (2) TG-IR combination

Thermogravimetric(TG) measurement was carried out at a heating speed of 10°C/min from room temperature to 1000°C in a N<sub>2</sub> flow of 35ml/min. The organic groups that desorbed from AMSA were distributed in N<sub>2</sub> flow, and they were measured by FTIR to assist the determination of successful modification. The same as in FTIR, the background data should also be measured for the next deduction.

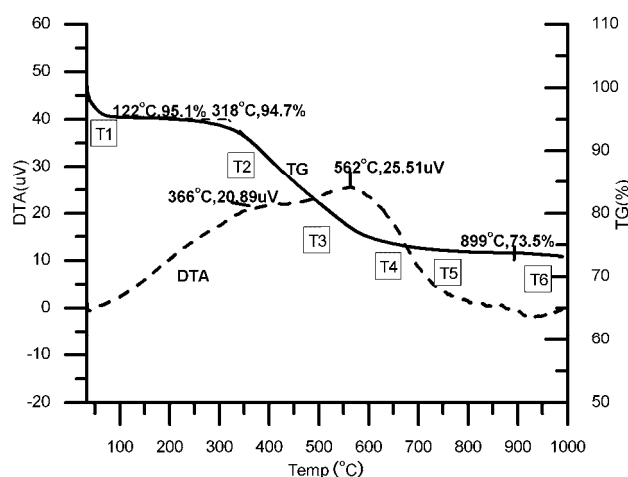


Fig. 3 TG/DTA results of AMSA from room temperature to 1000°C, where T1=120°C, T2=350°C, T3=500°C, T4=650°C, T5=750°C, T6=950°C.

TG experiment combined with FTIR detecting the groups desorbed from AMSA was also applied to identifying the APTES modification. Fig. 3 shows the TG-DTA result of AMSA. The 4.9% mass loss before 122°C is the escape of ethanol, water or gases absorbed in the air. A big 21.2% mass loss between 122°C and 899°C is the decomposition of  $-(\text{CH}_2)_3\text{NH}_2$  and  $-\text{OC}_2\text{H}_5$ .

The FTIR results, which stand for the characteristics of organic groups desorbed or decomposed from AMSA mixed in N<sub>2</sub> gas flow, were arranged from Fig.4(a) to Fig.4(f). The disturbance of CO<sub>2</sub> peaks in Fig.4(b)~Fig.4(f) are resulted from the deduction of the CO<sub>2</sub> background in the apparatus before the experiment. The differences between Fig.4(a) and Fig.4(b)~Fig.4(f) imply that AMSA absorbed CO<sub>2</sub> in the air in the room condition.

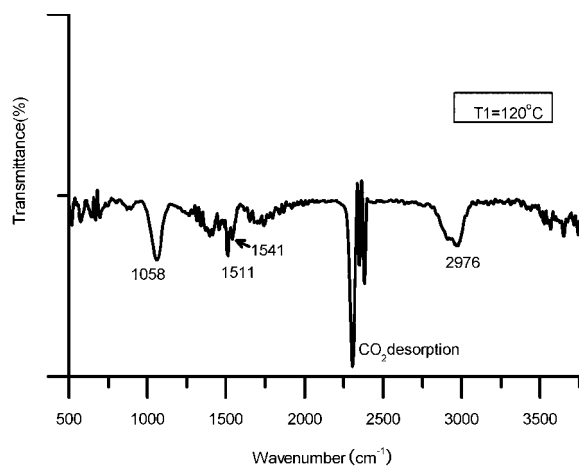


Fig. 4(a): T1=120°C. Wavenumbers of 1511cm<sup>-1</sup> and 1541cm<sup>-1</sup> which appears in the following figures are assigned to the background in detection.

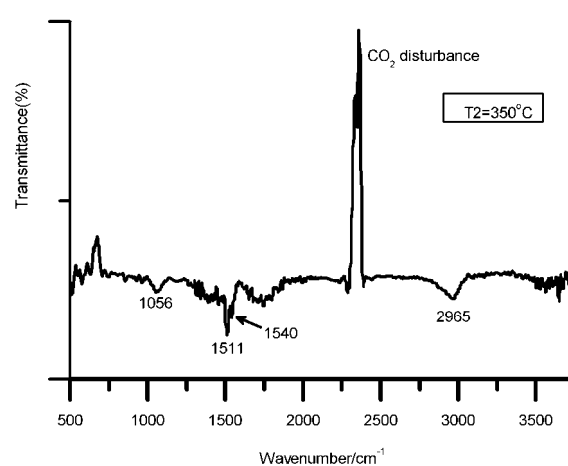


Fig. 4(b): T2=350°C. CO<sub>2</sub> disturbance which appears in the next following figures is due to the background deduction before the analysis, indicating the adsorption of CO<sub>2</sub> in Fig. 4(a).

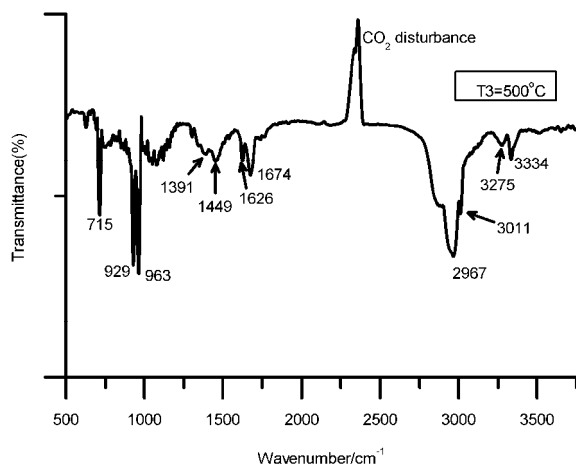


Fig. 4(c): T3=500°C. The breaking of C-N was determined by 3275cm<sup>-1</sup>, 3334cm<sup>-1</sup>, 1626cm<sup>-1</sup>, 1674cm<sup>-1</sup>; the C-C breaking could be identified by 1391cm<sup>-1</sup>, 3011cm<sup>-1</sup> for -CH<sub>3</sub>, and 1449cm<sup>-1</sup>, 2967cm<sup>-1</sup> for -CH<sub>2</sub>- as well.

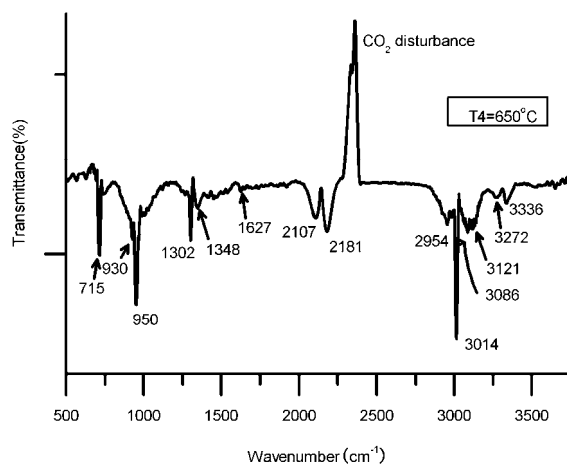


Fig. 4(d): T4=650°C. The unsaturated carbon bonds appeared due to the wave numbers of 2107cm<sup>-1</sup>, 2181cm<sup>-1</sup>, which could be attributed to the long chain breaking of -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-.

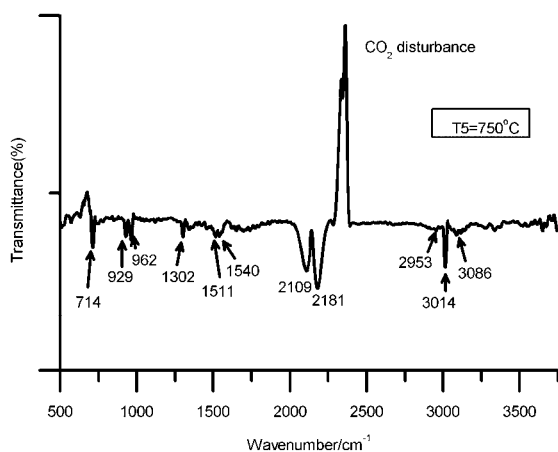


Fig. 4(e): T5=750°C. The similar results to Fig. 4(d) except the production of -NH<sub>x</sub>, where x=1 or 2.

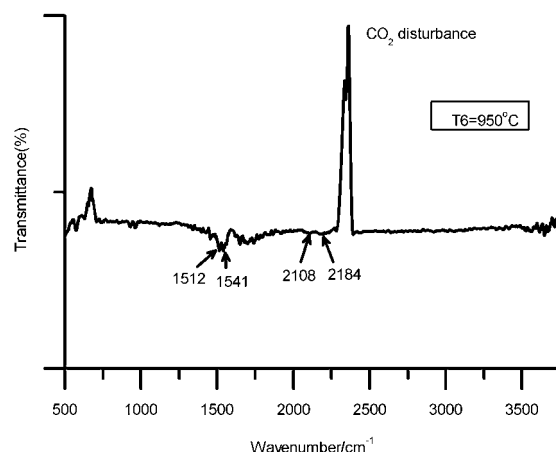


Fig. 4(f): T6=950°C, an end of the organic decomposition from AMSA.

Fig.4 FTIR characterization of groups released from the AMSA in TG experiment; the results indicated the components on AMSA surface

Fig.4(a) is the desorption of free ethanol according to the wavenumber of 1058cm<sup>-1</sup>and 2976 cm<sup>-1</sup>, and the CO<sub>2</sub> desorption assigned to 2300cm<sup>-1</sup>~2500cm<sup>-1</sup>. Fig.4(b) has a stronger adsorption and it should be the minute amount of -OC<sub>2</sub>H<sub>5</sub> decomposition from AMSA. Fig.4(c) shows a thermal bond breaking of C-N determined by the wavenumbers of 1625cm<sup>-1</sup>, 1674cm<sup>-1</sup>, 3275cm<sup>-1</sup>, and 3334 cm<sup>-1</sup>; unsaturated bond of -NH<sub>2</sub> shifts the adsorption peaks to higher wavenumbers. Adsorption wavenumbers at 2107cm<sup>-1</sup>, 2181cm<sup>-1</sup> and 3014cm<sup>-1</sup> in Fig.4(d) at

650°C is the characteristics of unsaturated bonds which can be assigned to -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>- cleavage; -C≡C- is probably produced. In Fig.4(e) -NH<sub>2</sub> is entirely decomposed from AMSA while the chain scission of -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>- is still in progress. When temperature reaches 950°C, the mass loss and decomposition stop. The results show a successful modification and a stable property for AMSA in N<sub>2</sub> below 300°C.

### (3) SEM with EDS

Samples' surface observation (only AMSA) was obtained by SEM with an accelerating voltage of 15KV with a scale of 1:30,000. A small cake was cut from the prepared sample to have a fresh surface with undamaged structure. Elements analysis except for hydrogen by EDS was used to estimate the content of nitrogen which is related to -NH<sub>2</sub>. Detailed information is given in table 1.

Table 1 Elements analysis of AMSA by EDS, an approximate atom percentage was given.

Element	k-ratio (calc.)	ZAF	Atom (%)	Element (Wt%)
C	0.0298	8.356	37.23	24.88
O	0.0535	4.921	29.60	26.35
Si	1.184	1.184	29.26	45.72
N	0.0038	7.974	3.91	3.04

Though nitrogen composes only 3.91% of all characterized atoms, its ratio to silicon is about 1:7. Carbon, which builds up the organic groups of -(CH<sub>2</sub>)<sub>3</sub>-NH<sub>2</sub> and -OC<sub>2</sub>H<sub>5</sub> in APTES and TEOS, is the most of all. Oxygen is considered a main content of the SiO<sub>2</sub> aerogel, including the remaining -OC<sub>2</sub>H<sub>5</sub> on the aerogel surface. The molar ratio of APTES to the source of TEOS was 1:2 in the preparation; that is a molar ratio of 1:3 for N and Si if APTES entirely grafted to the gel in the modification. The results indicate that some APTES remained in modification and escaped in drying process owing to the incomplete reaction and high drying temperature.

### (4) Characterization of surface area, pore volume, pore width.

Nitrogen adsorption-desorption isotherms both for PSA and AMSA were obtained on a Micromeritics ASAP-2000 sorptometer at N<sub>2</sub> liquid temperature. The samples were first dried at 120°C in pure N<sub>2</sub> flow for 1.5 hours. The surface area of the sample was calculated by BET method, and the pore size and distribution were obtained by BJH method.

N<sub>2</sub> adsorption-desorption isotherm results for PSA and AMSA are shown in Fig.5. The

adsorption between N<sub>2</sub> and the surface of SiO<sub>2</sub> aerogel is the multi-molecules adsorption in the beginning. When the pressure is close to the saturated vapor pressure, the adsorption curve is almost parallel to the Y axis; it is a classic performance of agglomeration between N<sub>2</sub> and solid particles. The adsorption and desorption curves breaks up at the middle relative pressure, showing that the pores in PSA and AMSA are open end to end.

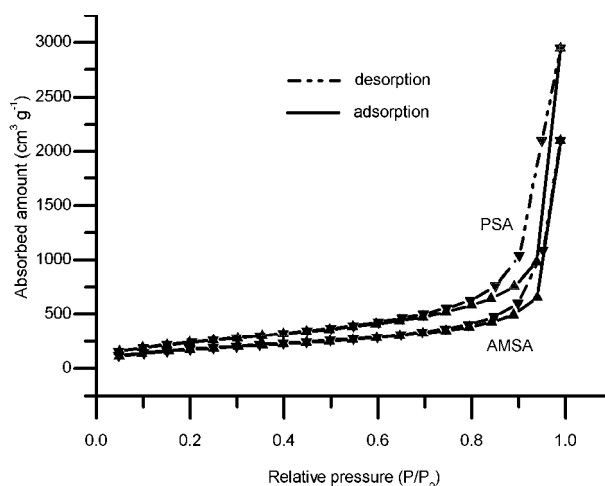


Fig.5 N<sub>2</sub> adsorption-desorption isotherms for PSA and AMSA

The surface area, pore volume, and mean pore width are listed in Table 2. Compared with PSA, the surface area and pore volume of AMSA decrease, which can be related to APTES modification; however, the mean pore widths are both about 20nm.

Table 2 Surface area, pore volume, and mean pore width of PSA and AMSA

	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Mean pore width (nm)
PSA	894.94	4.57	20.41
AMSA	628.45	3.25	20.71

Cumulative pore volumes of AMSA and PSA are shown in Fig.6. PSA has more pore volume whose pore width is less than 20nm than that of AMSA; it indicates that PSA should have more theoretical physical adsorption for gases. The results show that the maximal capacity of N<sub>2</sub> absorbed in AMSA is less than that of PSA; it is well accordant to the physical adsorption theory.

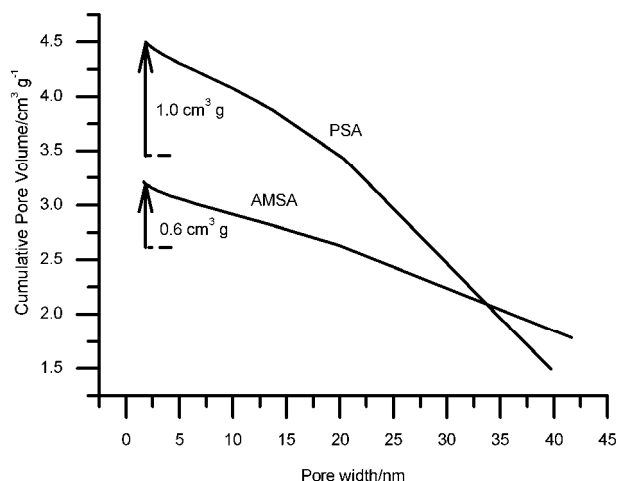


Fig. 6 Cumulative pore volume of PSA and AMSA: the “---” at the end of the arrows is a symbol where the pore width is 20nm.

### (5) FTIR:

The infrared spectra of the sorbents were recorded by FTIR spectrophotometer with dry *KBr* as the reference. Sorbents before and after adsorption were especially measured to make comparisons for the successful modification. Before the characterization, the background of the apparatus should be measured for the deduction.

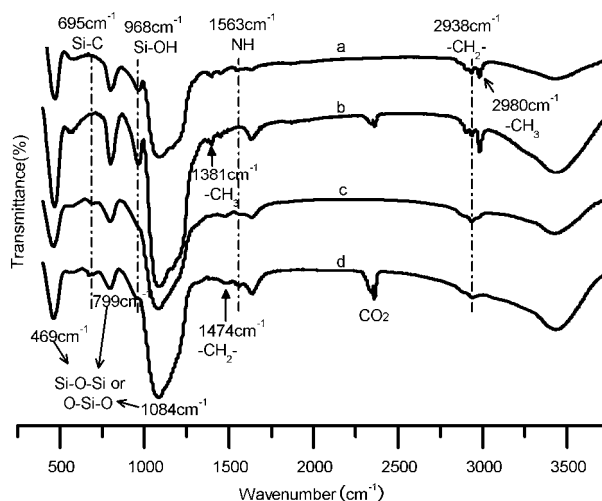


Fig. 7 FTIR analysis of PSA and AMSA, (a) and (b) described the PSA before and after CO<sub>2</sub> adsorption, respectively; (c) and (d) described the AMSA before and after CO<sub>2</sub> adsorption, respectively.

FTIR characterizations for PSA and AMSA before and after adsorption are shown in Fig.7. Wavenumbers at 1084 cm<sup>-1</sup>, 799 cm<sup>-1</sup> and 469 cm<sup>-1</sup> are the Characters of Si-O-Si and O-Si-O bonds. Adsorption peak at 2980 cm<sup>-1</sup> is the -CH<sub>3</sub> stretching vibration, and 1381 cm<sup>-1</sup> is the -CH<sub>3</sub> bending vibration, indicating the existence of -OCH<sub>2</sub>CH<sub>3</sub> on PSA surface. Wavenumber at

968cm<sup>-1</sup> is the Si-OH on PSA surface.

After modification -CH<sub>2</sub>- vibrations at 2938cm<sup>-1</sup> and 1474cm<sup>-1</sup> appear while -CH<sub>3</sub> adsorption peaks are weakened in the AMSA curves. In addition, according to the wavenumber at 695cm<sup>-1</sup> for Si-C, the disappearance of Si-OH in AMSA, and the N-H vibration at 1563cm<sup>-1</sup>, the successful modification of APTES is obvious.

#### 4. CO<sub>2</sub> adsorption measurement

The CO<sub>2</sub> adsorption measurements especially for AMSA were tested on the self-manufactured equipment which contains gas source, water steam generator, sample holder, and CO<sub>2</sub> concentration detector. The drawing is illustrated in Fig. 8.

The gas sources for experiments were 10.0% volume CO<sub>2</sub> and certain water vapor concentrations mixed in N<sub>2</sub> flow, with a flow rate of 0.3ml/min and 0.1g/min; the calculation is shown in the following “calculation steps”. The samples were first dried at 120°C in N<sub>2</sub> flow for at least 1.0 hour, and the desorption of CO<sub>2</sub> was undertaken at 85°C for at least 10 min. CO<sub>2</sub> adsorption capacities of AMSA were especially measured at 25°C and 50°C, respectively. Each experiment was repeated for 15 cycles to get an average.

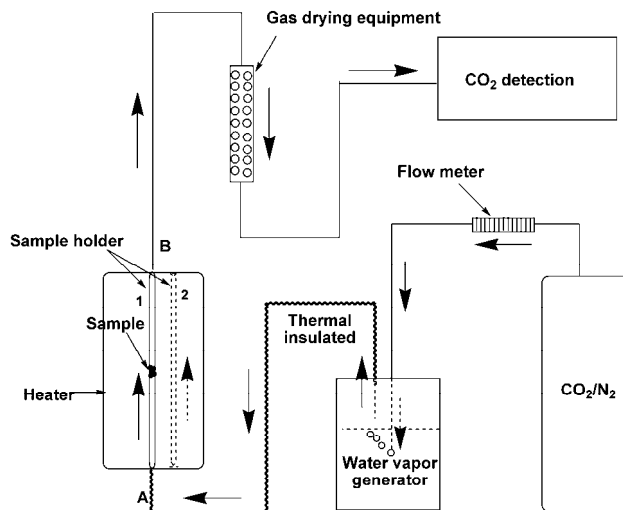


Fig. 8 Drawing of self-manufactured CO<sub>2</sub> adsorption measurement equipment.

The detailed apparatuses and the effects are shown as below:

- Gas source: 90%vol pure N<sub>2</sub> with 10%vol CO<sub>2</sub> are premixed before the experiment.
- Flow meter: flow meter is fixed to detect the flow rate from the source gas.
- Water vapor generator: water vapor volume concentration in mixed N<sub>2</sub>/CO<sub>2</sub> gas can be controlled by heating water at certain temperature.



- d. Thermal insulation: thermal insulation materials are used to keep the temperature of the mixed gases from generator.
- e. Heater: F21135 tube furnace (Barnstead International, Dubuque, IA), sample holder is fixed in and the temperature of adsorption can be easily controlled.
- f. Sample holder: a quartz tubular reactor with quartz wool as the bed holder inside is fixed to the heater; samples are placed on the quartz wool.
- g. Gas drying equipment: the drying medium for the adsorption of water in CO<sub>2</sub> can be anhydrous Calcium chloride or anhydrous magnesium sulfate;
- h. CO<sub>2</sub> detector: ZRE Infrared Gas Analyzer (Fuji Electric system Co. Ltd., Tokyo, Japan), and the data is collected by Data-Chart 3000 (Monarch Instrument Inc., Amherst, NH)

The detail procedure of the measurement is as follows:

- Special gas source with a certain ratio CO<sub>2</sub> and N<sub>2</sub> (10 vol% CO<sub>2</sub> and 90 vol% N<sub>2</sub> in our experiment) is premixed. A gas flow meter is fixed between the Gas source and Water vapor generator to measure the outlet gas flow.
- CO<sub>2</sub> adsorption measurement: a quartz tubular reactor with quartz wool (titled 1) as the bed holder is fixed in the heater. Preheat the heater to the desired temperature till it is stable. As is shown in figure 8, the ends of A and B are firstly connected to the dashed reactor (titled 2) to get the saturated adsorption for the apparatus. When the concentration detected by the CO<sub>2</sub> detection is equal to that of source gas, connect A and B to the reactor “1” immediately and then start to record the CO<sub>2</sub> concentration. The blank adsorption is also recorded for the deduction of adsorption capacities.
- Calculation steps:

We divide adsorption time  $t$  into  $\Delta t$  on average, and suppose that  $t=n\Delta t$  when we calculate the remaining content of CO<sub>2</sub>.

The division and calculation are demonstrated as follows:

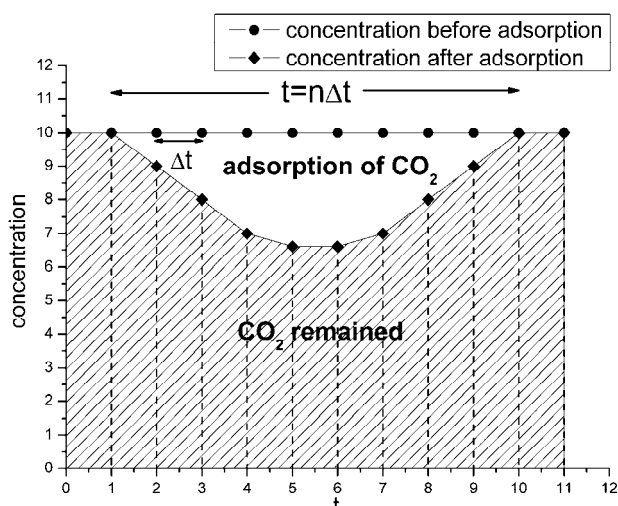


Fig. 9 Division of the original recorded data when calculation

Suppose the gases from the source gas are ideal gases, then CO<sub>2</sub> in the mixed gases is

$$PV = nRT = \frac{m_{CO_2}}{M_{CO_2}} RT = Pv \cdot t \cdot 10\% \quad (1)$$

$P$  : gas pressure from the source gases.

$V$  : volume of CO<sub>2</sub>

$n$  : molar of CO<sub>2</sub>

$R$  : 8.314472 kPa·L·mol<sup>-1</sup>·K<sup>-1</sup>

$T$  : experimental temperature(K)

$M_{CO_2}$  : molar mass of CO<sub>2</sub>

$v$  : flow rate of the gas fed by the source gas, 0.3L/min in our experiment

$m_{CO_2}$  : mass of outlet CO<sub>2</sub> from the source gases in a period of  $t$  and it can be controlled by changing  $T$ ,  $P$ , and  $v$ . In our experiment, we controlled it as 0.1g CO<sub>2</sub> per minute.

10%: volume concentration of CO<sub>2</sub> in mixture gases before adsorption

Thus we got a constant in our experiment

$$\frac{P \cdot v \cdot M_{CO_2}}{RT} = \frac{m_{CO_2}}{t \cdot 10\%} = \frac{0.1g / \min}{10\%} \quad (2)$$

Equation (2) shows the CO<sub>2</sub> before passing through the gas flow meter, and the product of  $P \cdot v$  in the experiment keeps a constant if the detected gas temperature equals to that of gas source.

Suppose that  $P'$  and  $v'$  are the outlet gas pressure and flow rate from the gas flow meter, as the concentration of CO<sub>2</sub> in mixed gases retains the constant, thus

$$\frac{P' \cdot v' \cdot M_{CO_2}}{RT} = \frac{m_{CO_2}}{t \cdot 10\%} = \frac{0.1g / \min}{10\%} \quad (3)$$

Suppose that  $dV_i$  and  $dm_{iCO_2}$  are the volume and mass of the remaining CO<sub>2</sub> in a period of  $dt$  at the exact time  $t_i$ , and  $x_i\%$  and  $v_i$  are the volume concentration and gas speed, respectively.

Because the detecting pressure is controlled the same as the pressure from the flow meter,

$$P' \cdot dV_i = P' \cdot x_i\% \cdot v_i \cdot dt = dn_i \cdot R \cdot T = \frac{dm_{iCO_2}}{M_{CO_2}} \cdot R \cdot T \quad (4)$$

$$dm_{iCO_2} = \frac{P' \cdot x_i\% \cdot v_i \cdot M_{CO_2} \cdot dt}{RT} \quad (5)$$

because  $v_i = v'$ ,

$$dm_{iCO_2} = \frac{P' \cdot x_i\% \cdot v_i \cdot M_{CO_2} \cdot dt}{RT} = 0.1(g / \min) \cdot \frac{x_i\% \cdot dt}{10\%} \quad (6)$$

we can also identify the remaining CO<sub>2</sub> at  $t_i$  during the period of  $\Delta t$

$$\Delta m_{iCO_2} = \frac{P' \cdot x_i\% \cdot v_i \cdot M_{CO_2} \cdot \Delta t}{RT} = 0.1(g / \min) \cdot \frac{x_i\% \cdot \Delta t}{10\%} \quad (7)$$

Thus, the CO<sub>2</sub> adsorption capacity at  $t_i$  in  $\Delta t$  can be written as:

$$m_{iCO_2}^a = 0.01 \cdot (10 - x_i) \cdot \Delta t \quad (8)$$

and the total adsorption capacity of CO<sub>2</sub> at  $t_i$  is

$$m_{i\text{CO}_2}^a = 0.01 \cdot \sum_1^i (10 - x_i) \cdot \Delta t \quad (9)$$

$m_{i\text{CO}_2}^a$  in equation (9) includes the adsorption by sorbent and bed holder (blank adsorption), so we should subtract the blank adsorption to get the real capacity of the sorbent.

- Regeneration of AMSA with 10% volume water vapor and 10% CO<sub>2</sub> in pure N<sub>2</sub> flow.

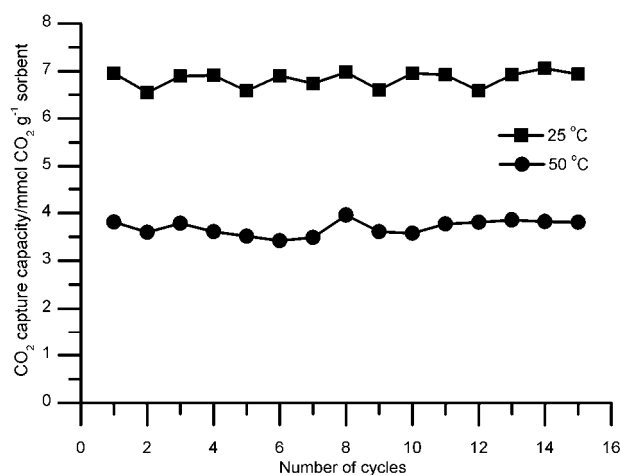


Fig.10 Adsorption properties of 15 cycles for AMSA with the mixed gases of 10.0%vol water vapor in 10%vol CO<sub>2</sub> and 90% N<sub>2</sub> gases