



## Functionalization with four different organic amines of mesoporous molecular sieves MCM-41 for CO<sub>2</sub> capture

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### ABSTRACT

First, mesoporous molecular sieves MCM-41 with channel rules were synthesized in a hydrochloric acid solution. And then, functionalized MCM-41 materials have been obtained by a incipient wetness impregnation method using four different organic amines, which were monoethanolamine(MEA), diethanolamine(DEA), diethylene triamine(DETA) and tetraethylenepentamine(TEPA). The samples were characterized by powder X-ray diffraction(XRD) and infrared spectroscopy (FT-IR). According to the XRD and FT-IR results, these samples were all loaded with organic amines successfully. The CO<sub>2</sub> static saturated adsorption capacity of these materials were found to depend on the kinds and amounts of the organic compound loaded. The strongest adsorption capacity of the four organic amines were all in a loading nearly 60%. Among them, the loading of TEPA has the best adsorption performance. These amine-loaded mesoporous molecular sieves MCM-41 could have great potential application to adsorb CO<sub>2</sub> in natural gas purification process.

**Keywords:** MCM-41; Organic amine; CO<sub>2</sub>; Adsorption capacity; Amine efficiency

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### INTRODUCTION

Nowadays, because of the excessive emissions of harmful greenhouse gases, such as CO<sub>2</sub>, CH<sub>4</sub>, the greenhouse effect is getting worse, which become a global concerns and a serious environmental challenge[1]. According to World Meteorological Organizaton, CO<sub>2</sub> concentration in atmosphere increased from 280 ppm by volume in pre-industrial times to 397.3 ppm in 2013. CO<sub>2</sub> capture and storage (CCS) technologies is an effective means of reducing CO<sub>2</sub>, in which the capture cost of CO<sub>2</sub> is about 75% of the total cost of CCS. There are a number of ways to separate CO<sub>2</sub> from gas mixtures, and adsorption is considered as potential one due to its low energy consumption and simple operation. In this regard, many novel CO<sub>2</sub> adsorbents are being researched, and considerable attention is being paid to mesoporous silicas because of their large surface areas, uniform mesopores, and tunable pore size[2,3].

At present, all commercial CO<sub>2</sub> removal techniques are based on the traditional MEA wet wash of chemical solution absorption method[4]. The disadvantages of this technology include: the renewable energy consumption is very high, about 4.5 GJ·(kgCO<sub>2</sub>)<sup>-1</sup>; the solution has strong corrosion foe the reactor[5]. Adsorption in solid amine adsorbents is a magnetic alternative technique recently applied for CO<sub>2</sub> capturing, which gets over the limitations of traditional technologies, in that the high adsorption capacity of CO<sub>2</sub>, the energy consumption greatly reduced and the corrosion of reactor is also getting degrees of lower[6]. According to the distinct preparation process of solid amine adsorbents, it can be divided into chemically grafting method and physical impregnation method[7]. The physical impregnation method has good points on easy to synthesis and high CO<sub>2</sub> adsorption capability, which is widespread applicated[8]. In recent years, the research literatures on solid amine adsorbents are relatively hot, which are mainly aimed at the influence of amine species and carrier structures on the properties of solid amine[9].

In this study, an acid solution synthesis method is used to prepare mesoporous molecular sieves MCM-41. Compared to the traditional alkali solution synthesis method[10], the advantage of which is without the need for high temperature reactor, and high-quality mesoporous molecular sieve can be obtained in a lower temperature and shorter time. Consequently, the objective of this work is to study the influence of the kinds and amine loadings of organic amines on the CO<sub>2</sub> static saturated adsorption capacity and amine efficiency, and the cyclic stability of solid amine adsorbents with four different organic amines.

## EXPERIMENTAL SECTION

### 1.1 Materials and Chemicals

In the present work, the methanol(99.5%), hydrochloric acid(36%-38%), tetraethyl orthosilicate(TEOS)(98%), monoethanolamine(MEA)(98%), diethanolamine(DEA)(98%), diethylenetriamine(DETA)(98%) and tetraethylene pentamine(TEPA)(98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The cetyltrimethylammonium bromide(CTAB)(98%) was purchased from Aladdin Industrial Inc. The distilled water was self-made in laboratory.

### 1.2 Preparation of mesoporous silica MCM-41

In accordance with the traditional method of dilute acie to prepare 2mol/L hydrochloric acid solution. 2g CTAB was added to 100mL 2mol/L HCl solution with stirring in room temperature. After the solution turned clear, 12.4mL of TEOS was added to the system at a certain speed and it was allowed to mix for 3h. After that, the turbid solution was allowed to stand 48h under seal condition, to make the sample aging. Then, the solid product was recovered by filtration and washing with deionized H<sub>2</sub>O to neutrality, and dried at 80°C in the air blast dryer overnight. The template CTAB was removed from the solid products by calcining the samples at 550°C for 6h.

### 1.3 Amino-functionalization of mesoporous silica MCM-41

A certain volume of an organic amine (MEA, DEA, DETA, TEPA), which was calculated according to the quality of carrier (20%, 40%, 60%, 80%), was added to 60mL methanol and stirring evenly, for approximately 30min. After that, 10g mesoporous silica MCM-41 was pretreated at 80°C to remove physisorbed water, and then added into the mixture solution prepared above slowly. The reaction mixture was sealed and vigorously stirred under room temperature for 24h. Then, the solvent was removed on a rotary evaporator at 100°C and the remaining solid was dried at 80°C in the air blast dryer overnight.

### 1.4 Characterization

The mesoporous silica MCM-41 was characterized X-ray diffraction (XRD) and FT-IR spectra. The powder XRD patterns were collected on a Rigaku D/MAX-2500PC diffractometer operated at 40 kV and 40mA with nickel-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The diffraction data was recored in the  $2\theta$  range 2-10° with a step size of 0.02° and scan rate of 4°/min. The FT-IR spectra were recorded by a Nicolet 460 spectrometer using the KBr powder technique with diffuse reflectance sampling accessory at a resolution of 4 cm<sup>-1</sup> at room temperature.

### 1.5 CO<sub>2</sub> static saturated adsorption performance test

The static saturated adsorption performance of CO<sub>2</sub> was carried out at 25°C and atmospheric pressure with a quartz tubular down flow reactor (inner diameter 6mm). The solid amine adsorbents (2g, particle size=100-200 mesh) was placed in the reactor. The pure CO<sub>2</sub> after drying was fed into the reactor. The inlet gas flow rate was 30mL/min, controlled by a CO<sub>2</sub> mass flow controller(Beijing HORIBA METRON Instruments Co.,Ltd.). The CO<sub>2</sub> static saturated adsorption capacity and the amine efficiency[11] of the solid amine adsorbents is calculated by following Eqs.(1) and (2):

$$C_{CO_2} (\text{mmol} \cdot \text{g}^{-1}) = \frac{\Delta m}{44m_0} \quad (1)$$

$$E_N [ \text{molCO}_2 \cdot (\text{molN})^{-1} ] = \frac{M_{\text{organica mine}} C_{CO_2}}{xl / l + 1} \times 0.001 \quad (2)$$

Where,  $m_0$  is the initial mass of the solid amine adsorbents,  $\Delta m$  is the difference value between initial mass and final mass of the solid amine adsorbents,  $M_{\text{organica mine}}$  is the relative molecular mass of the organic amine,  $x$  is the N concentrations of the organic amine,  $l$  is the loadings of the organic amine.

The flow chart of CO<sub>2</sub> static saturated adsorption performance test is shown in the Fig.1 There are three sections are

inlet gas section (left), reaction section (middle) and equilibrium section (right), respectively.

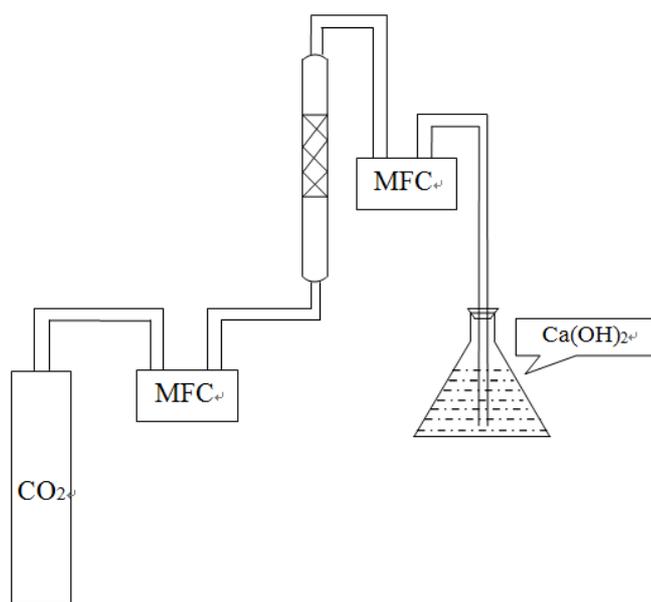


Fig.1 Flow chart of CO<sub>2</sub> static saturated adsorption performance test

## RESULTS AND DISCUSSION

### 2.1 FT-IR studies

The FT-IR spectra of bare and four different amine-modified mesoporous molecular sieves MCM-41 at same loading are shown in Fig.2. The bare MCM-41 molecular sieves exhibits a wide signal nearby  $3435\text{cm}^{-1}$  due to the O-H bond of the surface silanol groups. Studies[12] have shown that, the sharp peak at nearly  $1080\text{cm}^{-1}$  and  $800\text{cm}^{-1}$  is a characteristic IR adsorption peak of MCM-41 corresponding to the silicon-oxy tetrahedron stretching and bending vibrations respectively, and the adsorption peak near  $450\text{cm}^{-1}$  belongs to the bending vibrations of Si-O bond. The FT-IR spectra of amine-modified mesoporous molecular sieves MCM-41 demonstrates a signal at nearly  $1460\text{cm}^{-1}$  attributes to the scissor vibrations[13] of  $\text{NH}_2$ . The broad absorption peaks nearby  $3435\text{cm}^{-1}$  have increased completely indicates a possible overlap of peaks, which are stretching vibrations of N-H and O-H. The characteristic IR adsorption peaks of silicon-oxy tetrahedron are all weakened evidences the formation of hydrogen bonds between Si-O bond and OH groups in organic amines. Besides, the peaks presented in the range of  $1000\text{-}1250\text{cm}^{-1}$  became more broader, which may be the overlap of different absorption peaks. Therefore, physical impregnating of four different organic amines on MCM-41 molecular sieves are clearly established by comparing bare and modified molecular sieves' FT-IR spectra.

### 2.2 XRD studies

The powder XRD patterns of the calcined at  $500^\circ\text{C}$  mesoporous molecular sieves MCM-41 before and after modification with four different organic amines are shown in Fig.3. The bare mesoporous molecular sieves MCM-41 shows three characteristic diffraction peaks at  $2\theta$  values of 2.38, 4.12 and 5.06 which correspond to the planes (100), (110), and (200), respectively. After calcined at  $500^\circ\text{C}$ , the  $d_{100}$  diffraction peak is still existed, means that the structure still maintain at this point, which confirms the truth of the thermal stability of the mesoporous silica MCM-41 is better. After modification with organic amines, the  $d_{100}$  diffraction peak still exists, but extremely weak and shifts to the high-angle direction a little, which means that the XRD patterns of main pore structure are not changed significantly, though the vast majority of carrier channels are filled with organic amines. At the same time, the peaks at values of 4.12 and 5.06 pass off completely. The phenomenon is because the peak intensity depends on the scattering contrast between the pore channels and hole walls[14]. However, the scattering contrast always reduces after adhering of organic amine groups to the specific surface of MCM-41, which will weaken the peak intensity. In summary, for different organic amines are all loaded on the mesoporous molecular sieves MCM-41 successfully.

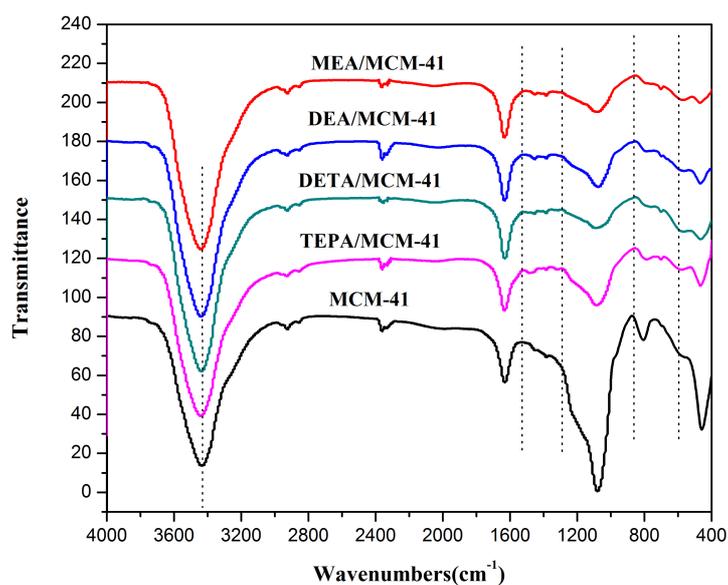


Fig.2 The FT-IR of solid amine adsorbents

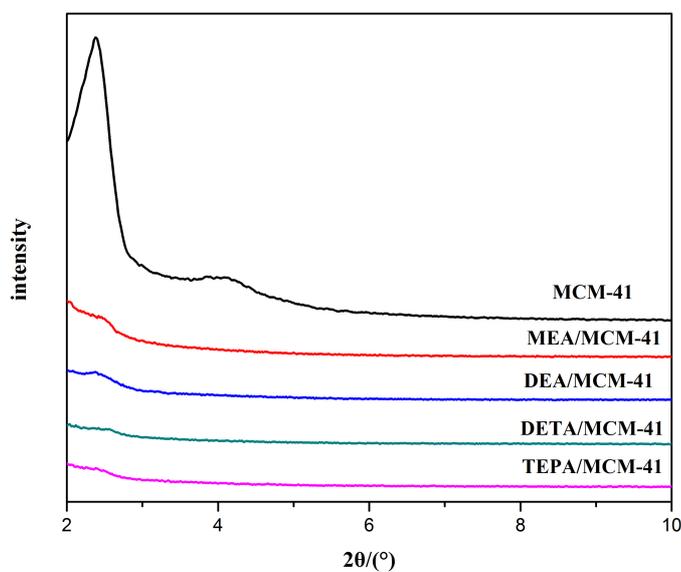
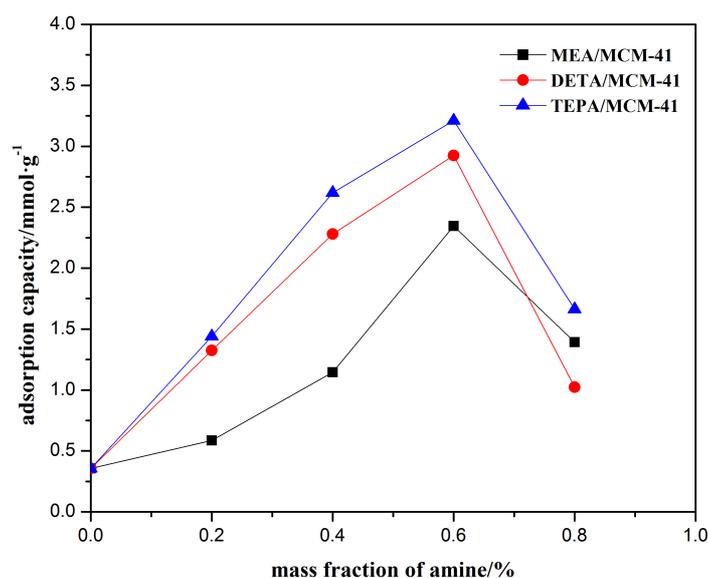


Fig.3 The XRD of mesoporous silica MCM-41

### 2.3 CO<sub>2</sub> static saturated adsorption performance test studies

#### 2.3.1 effects of organic amine molecule chain length

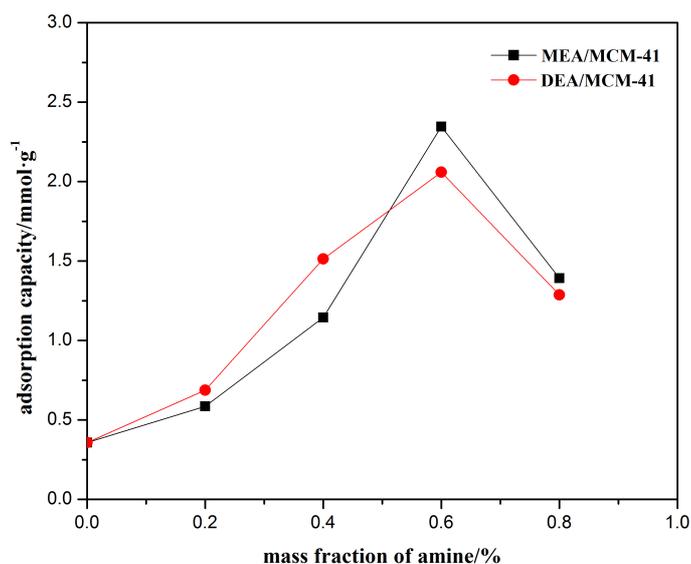
The three curves in Fig.4 are the adsorption properties of three solid amine adsorbents (MEA/MCM-41, DETA/MCM-41, TEPA/MCM-41) with the change of the amine loadings in the pure CO<sub>2</sub> at 25°C, among them, the amine loadings refer to the mass fraction of organic amine in solid amine adsorbents. It can be seen from Fig.4 that the maximum CO<sub>2</sub> static saturated adsorption capacity reached approximately at 2.3455mmol/g, 2.9250mmol/g and 3.2114mmol/g, which appears at the amine loading nearby 60%. Before the amine loading amount is 60%, the adsorption capacity increases rapidly with the increase of loading, and the increasing rate is related to the organic amine molecule chain length. Under the same loading, the longer the molecule chain length, the more contact points between organic amines and CO<sub>2</sub>. However, when the loading exceeds 60%, the surface of solid amine adsorbents cover a plethora of amine molecules, which block the carriers' inner holes and increase the mass transfer of gas molecules[15], thus the adsorption capacity begins to cut down gradually.



**Fig.4** CO<sub>2</sub> adsorption capacity of solid amine adsorbents  
(MEA/MCM-41 DETA/MCM-41 TEPA/MCM-41)

### 2.3.2 effects of OH groups

In Fig.5, it can be seen that two kinds of organic amines, containing different number of OH groups, are supported on the mesoporous silica MCM-41 with the change of the amine loadings. The adsorption properties of two solid amine adsorbents prepared above are tested in the pure CO<sub>2</sub> at 25°C. As shown in Fig.5, the maximum CO<sub>2</sub> static saturated adsorption capacity reached approximately at 2.3455 mmol/g, 2.0591 mmol/g, which appears at the amine loading nearby 60%. The maximum CO<sub>2</sub> saturated adsorption capacity of two solid amine adsorbents is not much difference, probably because per mole of organic amine contains an amine molecule. Nevertheless, at the beginning, the increasing rate of DEA/MCM-41 is faster than MEA/MCM-41, owing to the OH groups react with CO<sub>2</sub> to adsorb a part of CO<sub>2</sub>. In pace with the increasing of loading, the adsorption capacity of DEA/MCM-41 is lower than MEA/MCM-41, in that the CO<sub>2</sub> adsorption capacity of secondary amines are not stronger than primary amines[16] and the influence of OH groups on the adsorption capacity is not obvious. Similarly, due to the inner holes are blocked, the active site density decreased and reactive activity declined continuously, that the adsorption capacity cuts down after exceeding the 60% loading.



**Fig.5** CO<sub>2</sub> adsorption capacity of solid amine adsorbents  
(MEA/MCM-41 DEA/MCM-41)

### 2.3.3 amine efficiency of different organic amines

Amine efficiency refers to the average amount of CO<sub>2</sub> fixed by per mole N. Under anhydrous condition, the maximum adsorption amount of CO<sub>2</sub> by per mole N is 0.5mol, and the reactions of CO<sub>2</sub> with primary amines and secondary amines as the following Eqs.(3) and (4):



When the water exists, the maximum adsorption amount of CO<sub>2</sub> by per mole N is 1mol, and the reactions of CO<sub>2</sub> with primary amines and secondary amines as the following Eqs.(5) and (6):



As can be seen from Fig.6, amine efficiency increases at low carrying amount, explains that the load of organic amines has not too much effect on the pore structure of carrier, and the support surface also provides abundant active sites. After the active sites of carrier surface is occupied completely, with the increasing of the amine loading, the internal diffusion resistance of CO<sub>2</sub> grows gradually and becomes a controlling factor. While the adsorption capacity may still increase, but the actual amine efficiency is falling in that the loadings is raised.

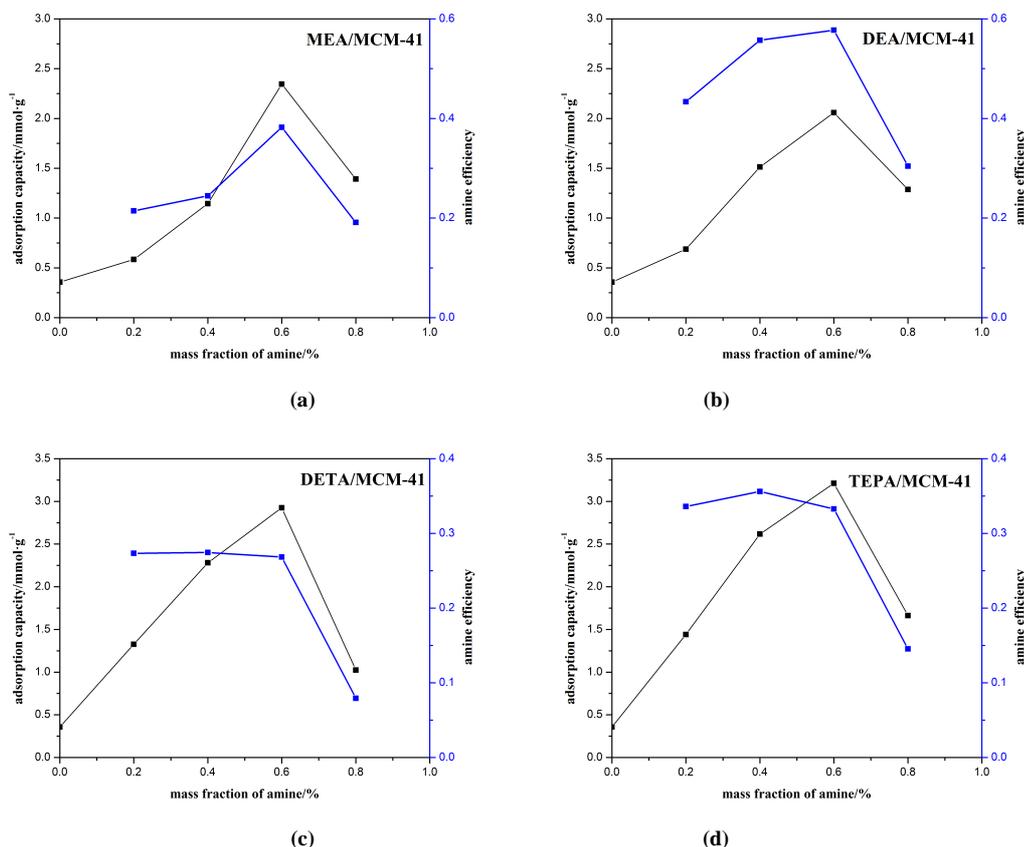


Fig.6 Amine efficiency of different organic amines

### 2.4 Cyclic stability

After reaching the saturation adsorption, these solid amine adsorbents placed in a vacuum drying oven at 120°C for desorbing 8h, and then repeated the above pure CO<sub>2</sub> adsorption experiment. The adsorption-desorption cycle tests were carried out for 10 times to determine the cycle stability of these solid amine adsorbents. The experimental results are shown in Fig.7 and Fig.8, which can be seen that in the first 5 cycles, the adsorption capacity of all adsorbents remain essentially unchanged. Adsorption capacity drops significantly from the sixth cycle, among them, the MEA/MCM-41 and DEA/MCM-41 is particularly obvious, and their total mass loss are about 12.99% and

10.02% respectively. In these four solid amine adsorbents, the adsorption capacity of TEPA/MCM-41 is the endsville, the total mass loss is just 4.02%. With the increasing number of cycle test, the adsorption capacity of the adsorbents will continue to decrease certainly. However, during the service life, the adsorbent can maintain in the range of the best adsorption capacity, which means that has a good parcticability and is pontential for long-term use.

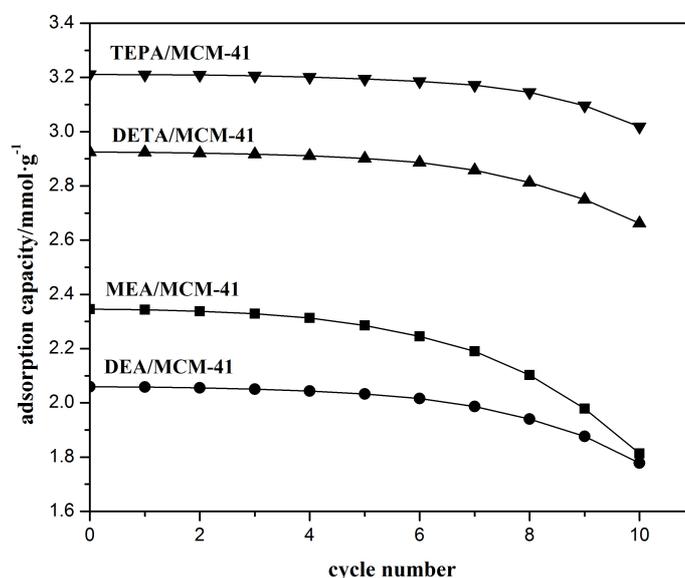


Fig.7 Adsorption capacity change with increase of cycle

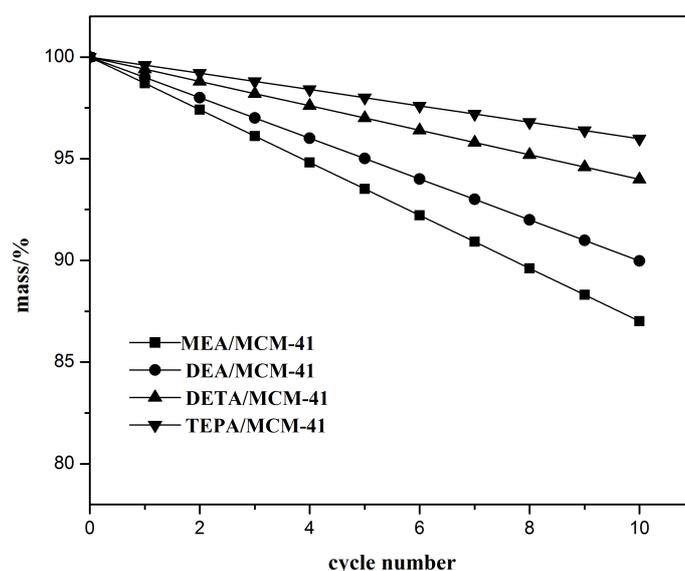


Fig.8 Mass loss of adsorbents at different cycles

## CONCLUSION

Room-temperature synthesized the mesoporous silica MCM-41 in hydrochloric acid solution, and modified with four different organic amines (MEA, DEA, DETA, TEPA) via physical impregnation method. According to FT-IR and XRD results, it can be recongnized that the organic amines are supported on the mesoporous molecular sieves MCM-41 successfully. After loading the organic amines, the maximum CO<sub>2</sub> static saturated adsorption capacity reached approximately at 2.3455mmol/g, 2.0591mmol/g, 2.9250mmol/g, 3.2114mmol/g separately. The cycle stability of these four solid amine adsorbents are all not bad, in which the adsorption capacity of TEPA/MCM-41 is the endsville and the total mass loss is just 4.02%.

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