



Capture of carbon dioxide by amine-impregnated as-synthesized MCM-41

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Abstract

The novel carbon dioxide (CO₂) adsorbents with a high capture efficiency were prepared through impregnating the as-synthesized MCM-41 with three kinds of amines, namely diethylenetriamine (DETA), triethylenetetramine (TETA) and 2-amino-2-methyl-1-propanol (AMP). The resultant samples were characterized by small angle X-ray diffraction and low temperature N₂ adsorption. The synthesis way not only saves the energy or extractor to remove the template but also is environmentally friendly due to the absence of the potential pollutants such as toluene. CO₂ capture was investigated in a dynamic packed column. The sample impregnated by TETA showed the highest adsorption capacity, approximately 2.22 mmol/g at 60°C due to its highest amino-groups content among the three amines. The CO₂ adsorption behavior was also investigated with the deactivation model, which showed an excellent prediction for the breakthrough curves.

Key words: CO₂ capture; as-synthesized MCM-41; impregnation; deactivation model

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Introduction

From 280 to 380 parts per million (ppm) has increased the atmospheric CO₂ concentration since the industrial age, which is likely responsible for a large part of the 0.6°C rise in the average global surface temperature over the past century (Service, 2004). The increased CO₂ is mainly due to the combustion of the vast amounts of fossil fuels. One feasible way to mitigate this trend is to capture CO₂ from flue gas with inexpensive adsorbents and then sequester it underground (Schiermeier, 2006). However, the most common adsorbents, such as zeolites (Takamura et al., 2001) show low CO₂ adsorption capacities at the elevated temperature due to physisorption. Although organically grafted mesoporous silicas (Hiyoshi et al., 2005; Kim et al., 2005; Knowles et al., 2005; Liu et al., 2007) show relatively high CO₂ adsorption capacities, they are still unsuitable, considering the requirement of the commercial adsorbents (Chang et al., 2003). On the other hand, the synthesis process of organically grafted mesoporous silicas not only consumes a large amount of energy but also unavoidably pollutes the environment due to the presence of the toluene or ethanol. A promising candidate is the as-synthesized MCM-41, which can avoid the pollution of toluene and dramatically improve the adsorption capacity of CO₂ when impregnated by amines.

MCM-41, known as one of the M41S mesoporous molecular sieve family, was initially discovered by Mobil

Corp. in 1992 (Kresge et al., 1992). It consists of uniform, hexagonal arrays of mesopores with pore openings between 1.5 and 10 nm. Synthesis of MCM-41 is based on the addition of an inorganic silica source (sodium silicate, tetraethoxysilane, fumed silica) to the solution containing the surfactant micellar template. In the final material the surfactant micelles are encapsulated in the silica skeleton, and this material is denoted as the as-synthesized MCM-41. When calcined or extracted to remove the template, the material is denoted as MCM-41. Some experiments demonstrated the adsorption of various substances, such as benzene, toluene and propan-1-ol by this as-synthesized MCM-41 whose pores were filled with organic template (Goworek et al., 2007; Vartuli et al., 2001). The introduction of tetraethylenepentamine (TEPA) into the as-synthesized SBA-15 containing template in the pores, as efficient CO₂ adsorbent was reported by Yue et al. (2006), their results showed CO₂ adsorption capacity as high as 173 mg/g. This is possibly enhanced by the hydroxyl groups in the template contained in the as-synthesized silica (Yue et al., 2006) or in the additives rich in hydroxyl groups (Satyapal et al., 2001; Xu et al., 2003). In the case of amine-impregnated as-synthesized MCM-41, the study is rarely reported.

The gas-solid reaction process, such as CO₂-hydrotalcite, can be well described by the linear driving force (LDF) model (Ding and Alpay, 2000). However, this model is difficult to use because of the large number of adjustable parameters with relation to the solid structure,

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to the product layer as well as the diffusion resistances. Another model, namely deactivation model, proposed in the literature was successful to predict the breakthrough curves of CO₂ (Ficicilar and Dogu, 2006) or H₂S (Yasyerli et al., 2001) in packed adsorption columns. However, deactivation model was not reported to simulate the breakthrough curves in CO₂ and amine-impregnated as-synthesized MCM-41 reactions.

In this work, the adsorption rate and capacity of CO₂ on the as-synthesized MCM-41 impregnated by various amines were investigated with the dynamic column method at 60°C, as the temperature of flue gas after desulphurization was mostly below 60°C. The adsorption rate and capacity of CO₂ was simulated with the deactivation model due to its simplicity.

1 Materials and methods

1.1 Materials

MCM-41, obtained from Hailong Mesoporous Molecular Sieves Company Ltd. (China) was synthesized according to the reported method (Beck et al., 1992; Kresge et al., 1992), but the template in the mesopore of MCM-41 was not removed here. The sample was denoted as as-synthesized MCM-41 and simplified as M in this article.

DETA (NH₂-CH₂CH₂-NH-CH₂CH₂-NH₂) and TETA (NH₂-CH₂CH₂-NH-CH₂CH₂-NH-CH₂CH₂-NH₂) were obtained from Hangzhou Chemical Reagent Company (China), and AMP (NH₂C(CH₃)₂-CH₂-OH) was from Aldrich (USA). The main physico-chemical properties of these amines are presented in Table 1. All the chemicals were used as received without further purification.

1.2 Preparation of the adsorbents

The amine-impregnated M (M-DETA, M-TETA and M-AMP) were prepared by impregnation adapted from other research groups (Liu et al., 2007). Briefly, dissolve 2.0 mL of amine in 20 mL of ethanol under mechanically stirring for 0.5 hr, then 2.0 g of M previously dried at 100°C was added into the mixture under stirring and refluxing for 2 hr, followed by elimination of ethanol on a water-bath at 80°C. The amine-impregnated samples were then dried in a natural convection oven at 100°C for 2 hr, and subsequently stored in capped vial until use.

1.3 Characterization of the samples

X-ray diffraction (XRD) measurements were performed on a Rigaku powder diffractometer (Rigaku, Japan) with Cu K_α radiation. The tube voltage was 45 kV, and the current was 40 mA. The XRD diffraction patterns were taken in the 2θ range of 0.5–10° at a scan speed of 2°/min.

Thermal gravimetric analysis and differential thermal

gravimetric analysis (TGA/DTG) were carried out with a DSC-TGA (SDT Q600, TA Instruments, USA) under dynamic N₂ atmosphere (120 mL/min) from room temperature to 600°C with a rate of 10°C/min.

Elemental analysis was carried out with Flash EA1112 (Thermo Finnigan Inc., Italy) to determine the amine content (wt.%) in the bulk amine-impregnated as-synthesized MCM-41. The amine content was defined as the number of nitrogen atoms per gram of the impregnated M.

N₂ physical adsorption isotherms were also employed to evaluate the textural change after impregnation, which were measured by BELSORP measuring instruments (BELSORP-mini II, Inc., Japan). Each sample was degassed at 100°C under nitrogen flow for 4 hr prior to measurement. The N₂ adsorption data were recorded at the liquid nitrogen temperature (−196°C). The surface areas were calculated using the Brunauer-Emmett-Teller equation. The total pore volume was calculated from the amount of adsorbed N₂ at the partial pressure $P/P_0 = 0.99$.

1.4 Carbon dioxide adsorption experiments

Carbon dioxide adsorption experiments were carried out by a dynamic packed column method using a binary mixture of 15 vol.% CO₂ (99.995%) in N₂ (99.999%). The typical procedure was as follows. Prior to the adsorption, the preweighed amine-impregnated M (1.5 g, 40–60 mesh powder) was packed in a Pyrex quartz tube with an inner diameter of 10 mm and a length of 250 mm, and heated at 100°C for 1 hr in a downstream of He flow (99.999%) at a rate of 41 mL/min, followed by cooling to the adsorption temperature, 60°C. He flow was then switched to the binary mixture at a rate of 41 or 70 mL/min until the adsorbent was saturated by CO₂. The breakthrough curve of CO₂ was obtained by analyzing the effluent gases with a gas chromatograph (GC-9750, Fuli Science Inc., China) equipped with a packed Porapak Q column (3 m × 3 mm outer diameter) and a TCD detector.

2 Results and discussion

2.1 Characterization of the materials

Figure 1 provides the low angle XRD patterns for M and amine-impregnated M. The major peaks of M were almost replicated by those of the amine-impregnated M, although the intensities of peaks decreased slightly and the peaks shifted to a little higher 2θ angles, similar to the results of other research groups (Plaza et al., 2007; Xu et al., 2003). These changes were possibly caused by the pore filling effect of the support channels and the amine coating on the outer surface of the support.

TGA and DTG data of M before and after impregnation by various amines are shown for the change in structure (Fig. 2). For M, DTG profile shows two mass loss peaks: the first peak with a mass loss of 2% below 100°C can be attributed to the moisture evolving, and the second peak with a mass loss of 38% near 280°C is due to the removal of the template. After impregnation by DETA, TETA or AMP, the first peaks intensities increased compared with

Table 1 Chemical properties of the amines used

Amine	Molecular weight	N content (wt.%)
DETA	103.17	40.7
TETA	146.24	36
AMP	89.14	15.7

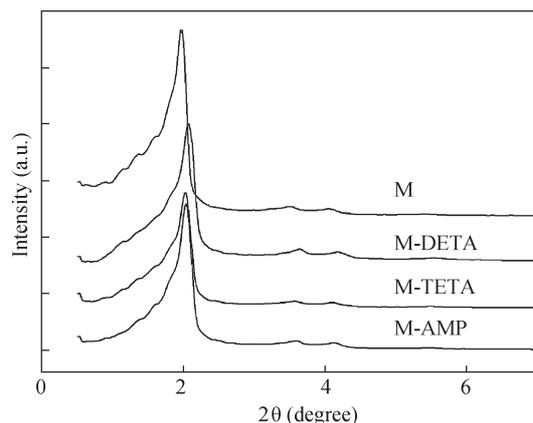


Fig. 1 Low angle XRD patterns for M and various amine-impregnated M. "M" represents as-synthesized MCM-41.

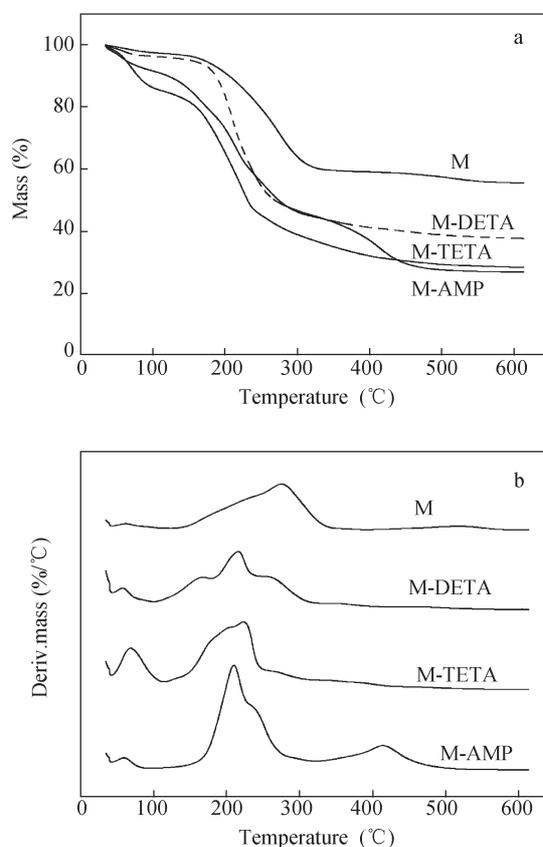


Fig. 2 TGA (a) and DTG (b) data of M before and after various amine impregnation.

that of M, because of the easy affinity of moisture and CO₂ impurities on them. The order of the first peaks intensities is M-TETA > M-DETA > M-AMP > M, because the base groups of amines decrease conversely (Table 2). After the encapsulation of the various amines, the second mass loss peaks with shoulders are observed, which is due to the simultaneous decomposition of the amines and the template. The last peak of M-AMP, may originate from the condensation of hydroxyl group of AMP. Similar result was observed at about 400°C by Liu et al. (2007), who used Triethanolamine (TEA, also with hydroxyl group in the molecule) as coating agent on SBA-15.

Table 2 Characterization details of the supports (MCM41 and M) and amine-impregnated Ma

Sample	Surface area (m ² /g)	Pore volume (mL/g)	N content (wt.%)	CO ₂ adsorption capacity* (mmol/g)
MCM-41	669.7	0.60	–	–
M	27.0	0.10	–	–
M-DETA	8.1	0.012	10.60	1.87
M-TETA	3.4	0.0048	14.80	2.22
M-AMP	2.2	0.0029	5.82	1.14

* CO₂ adsorption capacity was determined at 60°C.

In summary, the amine-impregnated M showed stability up to 110°C. Therefore, they can be regenerated at 100°C without decomposition.

Figure 3 shows the N₂ adsorption isotherms of M and amine-impregnated M. The surface areas, total pore volumes and nitrogen contents were calculated. The results are listed in Table 2. M shows much lower surface area and pore volume than MCM-41, which is caused by the residual template in the channels, about 38% by weight. After M was impregnated by amines, the surface area and the pore volume decreased dramatically. The pore volume of the amine-impregnated M may originate from the residual pores and the newly formed pore structure in the aggregated particles (Yue et al., 2006). Similar results can be seen in the previous studies (Jadhav et al., 2007; Plaza et al., 2007; Son et al., 2008).

2.2 CO₂ adsorption

Typical experimental breakthrough curves of CO₂ at the effluence are given in Fig. 4. All the amine-impregnated M seemed to follow the similar adsorption pattern. As seen in Fig. 4a, no CO₂ was detected in the effluence due to the complete adsorption in the initial step. With adsorption going on, the CO₂ concentration of the effluence increases gradually to the feeding level. Breakthrough time of CO₂ are in the following order: M-AMP < M-DETA < M-TETA. The ratio of C/C₀, was introduced to reflect the gradual increase of the CO₂ concentration of the effluence, where C and C₀ referred to the CO₂ concentrations in the effluence and influence, respectively. The C/C₀ ratio gradually reaches 1 when the adsorbent was saturated by

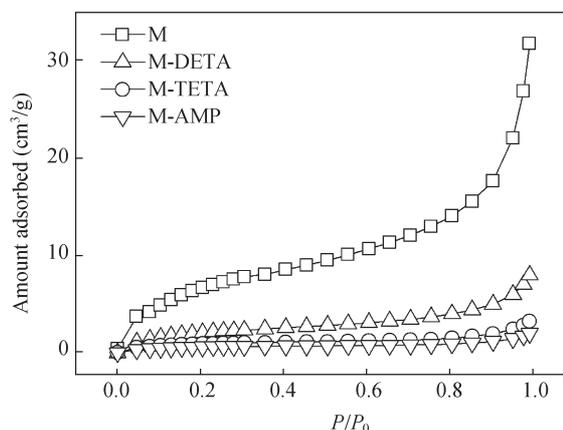


Fig. 3 N₂ adsorption isotherms of M and amine-impregnated M. "M" represents as-synthesized MCM-41.

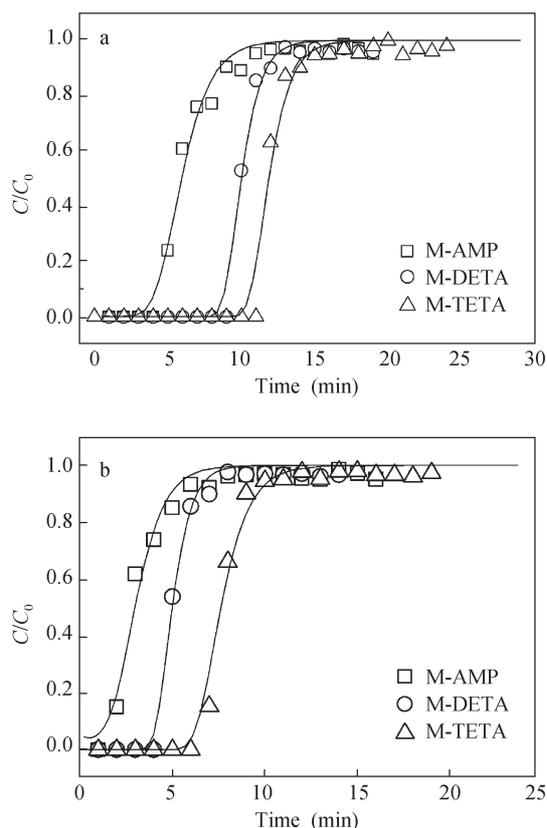


Fig. 4 Experimental breakthrough data of CO₂ and simulated breakthrough curves of amine-impregnated as-synthesized MCM-41 at 41 mL/min (a) and 70 mL/min (b).

CO₂. The adsorption capacity was obtained by integrating the area of the simulated curve.

The adsorption capacities of amine-impregnated M are listed in Table 2. The order of the adsorption capacities is M-TETA > M-DETA > M-AMP, the highest adsorption capacity is 2.22 mmol/g for M-TETA, which is comparable to those of SBA-15 and HMS grafted by aminosilane (Hiyoshi et al., 2005; Knowles et al., 2005) (Table 3). However, in the preparation process of amino group-grafted SBA-15 and HMS, the templates need to be removed by calcination at 550°C for 5 hr. Therefore, much energy was consumed. At the same time, toluene was used to solve TA, which could be harmful to the human health and unfriendly to the environment. In our study, it is obviously of great advantages in the viewpoints of energy consuming and environment protection.

On the other hand, CO₂ fixation on M impregnated by the primary amine is expected to take place through the

following Reaction (1).



where, *R* is an alkyl group.

While for CO₂ adsorption on M impregnated by the secondary amine, it follows Reaction (2).



From Reactions (1) and (2) it can be seen that whether for the primary amine or the secondary amine, one mole of CO₂ reacts with every two moles of the primary amines or the secondary amines. Therefore, the CO₂ adsorption capacities depend on the amounts of the amino-groups: the more the amino-groups, the higher the CO₂ adsorption capacities. The order of the amino-groups contents of the three amine-impregnated samples is M-TETA > M-DETA > M-AMP, as shown in Table 2 as the form of the nitrogen contents. Therefore, M-TETA shows the highest CO₂ adsorption capacity, M-DETA the second, and M-AMP the lowest.

2.3 Modeling of CO₂ adsorption

The adsorption of CO₂ on the amine-impregnated M is more likely a chemisorption or gas-solid non-catalytic reaction than a simple physisorption, which involves a number of steps, such as CO₂ diffusion into the surface and pores, reaction with the active sites, and formation of a product layer over the surface or pore walls. With the adsorption going on, changes in the pore structure and in the active surface area are expected. Additionally, formation of the product layer also creates penetration resistance for the transport of CO₂ to the active sites of the adsorbents. Therefore, all these factors seem to result in the gradual deactivation of the adsorbents.

In the deactivation model, an activity term *a* is introduced into the rate expression to represent the deactivation due to the decrease of the active site concentration, the textural changes and so forth. With the assumption of the pseudo steady state and neglecting of the axial dispersion term (Wang et al., 2008; Yasyerli et al., 2001), the species conservation equation for CO₂ concentration in the dynamic packed column and the rate equation for the activity change of the solid reactant with time are shown as following Eqs. (3) and (4):

$$-Q \frac{dC_A}{dW} - k_0 C_A \quad a = 0 \quad (3)$$

$$-\frac{da}{dt} = k_d C_A^n a^m \quad (4)$$

Table 3 CO₂ adsorption data of amine modified silica

Adsorbent	Temperature (°C)	CO ₂ partial pressure (kPa)	Capacity (mmol/g)	Reference
Propylethylenediamine-SBA-15	60	15	1.36	Hiyoshi et al., 2005
Propylethylenetriamine-MCM-41	25	5.1	0.97	Harlick and Sayari, 2006
Aminopropyl-MCM-48	25	5	1.13	Huang et al., 2003
Aminopropyl-HMS	20	90	1.6	Knowles et al., 2005
Propylethylenediamine-SBA-16	60	15	0.727	Wei et al., 2008
M-TETA	60	15	2.22	This study

where, Q (mL/min) is the volumetric flow rate; C_A (%) is the CO_2 concentration in the effluence; W (g) is the adsorbent mass; k_0 (mL/(min·g)) is the initial adsorption rate constant; a is the activity of the amine-impregnated M; t (min) is time; k_d (min^{-1}) is the deactivation rate constant.

Generally, the deactivation rate is expected depending on the first order of CO_2 concentration ($n = 1$) and also on the activity itself ($m = 1$) (Ficilar and Dogu, 2006; Yasyerli et al., 2001). Therefore, the analytical solution of this model gives the following Eq. (5) for the breakthrough curves:

$$\frac{C_A}{C_{A0}} = \exp\left(\frac{1 - \exp((k_0 W/Q)(1 - \exp(-k_d t)))}{1 - \exp(-k_d t)}\right) \exp(-k_d t) \quad (5)$$

Through the non-linear regression analysis of the experimental breakthrough data from the adsorption of CO_2 on the amine-impregnated M at 41 and 70 mL/min, the two parameters were obtained, k_0 and k_d , as listed in Table 4. The prediction of the deactivation model shows good agreement with the experimental data either at 41 mL/min or at 70 mL/min since the correlation coefficient R^2 is higher than 0.97 in all cases. From Table 4, it seems that the deactivation model is stable and independent of the mixed gas flow rate. For M-DETA and M-TETA both the initial adsorption rate constant k_0 and the deactivation rate constant k_d are quite large, with the average values of k_0 and k_d being 320.9 mL/(min·g) and 1.04 min^{-1} , respectively. However, the constant k_0 of M-AMP is much lower than the average value, being consistent with its lowest CO_2 adsorption capacity.

Table 4 Initial adsorption rate constant and deactivation rate constant of CO_2 on the amine-impregnated as-synthesized MCM-41 at 41 and 70 mL/min

Sample	k_0 (mL/(min·g))	k_d (min^{-1})	R^2
Rate at 41 mL/min			
M-DETA	309.3	1.09	0.9856
M-TETA	332.4	0.98	0.9928
M-AMP	121.9	0.75	0.9886
Rate at 70 mL/min			
M-DETA	312.1	0.94	0.9961
M-TETA	328.9	0.97	0.9915
M-AMP	122.1	0.97	0.9719

3 Conclusions

The amine-impregnated as-synthesized MCM-41 were found to be attractive adsorbents for the CO_2 capture. The adsorption capacity was determined as high as 2.22 mmol/g at 60°C for M-TETA due to its highest amino-groups content. The method of impregnating as-synthesized MCM-41 with amines not only saves energy for template removal but also avoids the pollution of toluene in the grafting method. The deactivation model was used to simulate the CO_2 breakthrough curves of the dynamic column absorber and showed an excellent representation.

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