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## The dynamic $\text{CO}_2$ adsorption of polyethylene polyamine-loaded MCM-41 before and after methoxypolyethylene glycol codispersion†

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To reduce the cost of  $\text{CO}_2$  capture, polyethylene polyamine (PEPA), with a high amino density and relatively low price, was loaded into MCM-41 to prepare solid sorbents for  $\text{CO}_2$  capture from flue gases. In addition, methoxypolyethylene glycol (MPEG) was codispersed and coimpregnated with PEPA to prepare composite sorbents. The pore structures, surface functional groups, adsorption and regeneration properties for the sorbents were measured and characterized. When  $\text{CO}_2$  concentration is 15%, for 30, 40 and 50 wt% PEPA-loaded MCM-41, the equilibrium adsorption capacities were respectively determined to be 1.15, 1.47 and 1.66  $\text{mmol g}^{-1}$  at 60 °C; for 30 wt% PEPA and 20 wt% MPEG, 40 wt% PEPA and 10 wt% MPEG, and 50 wt% PEPA and 5 wt% MPEG codispersed MCM-41, the equilibrium adsorption capacities were respectively determined to be 1.97, 2.22 and 2.25  $\text{mmol g}^{-1}$  at 60 °C; the breakthrough and equilibrium adsorption capacities for 50 wt% PEPA and 5 wt% MPEG codispersed MCM-41 respectively reached 2.01 and 2.39  $\text{mmol g}^{-1}$  at 50 °C, all values showed a significant increase compared to PEPA-modified MCM-41. After 10 regenerations, the equilibrium adsorption capacity for codispersed MCM-41 was reduced by 5.0%, with the regeneration performance being better than that of PEPA-loaded MCM-41, which was reduced by 7.8%. The  $\text{CO}_2$ -TPD results indicated that the mutual interactions between PEPA and MPEG might change basic sites in MCM-41, thereby facilitating active site exposure and  $\text{CO}_2$  adsorption.

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## 1. Introduction

Coal-fired power plants are undoubtedly large  $\text{CO}_2$  emission points all over the world, in which the capture of  $\text{CO}_2$  has been extensively researched; Bui *et al.* has reviewed the progress for carbon capture and storage (CCS) and pointed out the way forward.<sup>1–3</sup> Solid amine adsorption technology, with weak corrosivity, highly efficient adsorption performance and low regeneration energy consumption, is recognized as an effective method.<sup>4–7</sup>

So far the study of amine-loaded solid sorbents mainly focuses on immobilizing amines onto the inner surface of porous supporting materials, such as metal-organic frameworks (MOFs),<sup>8–13</sup> mesoporous molecular sieves,<sup>14–22</sup> silicas<sup>23–31</sup> and so on.<sup>32–40</sup> Chen *et al.* incorporated polyethyleneimine (PEI) into mesoporous zeolite 13X prepared by pore-expanding original micropores; due to PEI-dispersion in mesopores, the  $\text{CO}_2$

adsorption capacity for PEI-modified 13X reached 80  $\text{mg g}^{-1}$  at 100 °C under a pure  $\text{CO}_2$  atmosphere.<sup>16</sup> Saha immobilized PEI in silicas and polymethyl methacrylate (PMMA) to prepare type I adsorbents, grafted different amounts of aminosilanes in mesoporous SBA-15 to prepare type II adsorbents and performed breakthrough adsorption experiments. Both sorbents showed significant adsorption capacities and consistent regenerability during 3–5 adsorption–desorption cycles.<sup>5</sup> Cheng *et al.* incorporated amines into silicas with trimodal pore structures, and the nanocomposite sorbents suggested rapid adsorption kinetics and good adsorption performance, with an adsorption capacity of 172  $\text{mg g}^{-1}$  being obtained for an amine loading amount of 70 wt%.<sup>25</sup> To further improve the dispersion and stability of TEPA or PEI with high viscosity, auxiliary reagents with hydroxyl or ether groups were coloaded into supporting materials for preparing composite sorbents.<sup>41–44</sup> Jung *et al.* coimpregnated PEI and 1,3-butadienediepoxyde (BDDE) with hydroxyl groups in silicas to investigate the improved  $\text{CO}_2$  adsorption performance of PEI-loaded silicas, which was primarily attributed to following two aspects. On the one hand, synergistic combinations between hydroxyl groups and the PEI on the inner surface of the supporting materials occurred, which promoted the dispersion and thermostability of PEI in silicas. On the other hand, after coimpregnation, the chemisorption ratio for amine and  $\text{CO}_2$  molecules changed

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from 2 : 1 to 1 : 1, and the  $\text{CO}_2$  adsorption efficiency improved.<sup>41</sup> Mafra *et al.* performed two-dimensional solid-state nuclear magnetic resonance (NMR) experiments on amine-modified silicas after adsorbing  $\text{CO}_2$ ; the results showed that all chemisorbed  $\text{CO}_2$  molecules participated in hydrogen bonding interactions with either neighboring alkylamines or surface silanols, and the work helped one to understand the configuration of chemisorbed  $\text{CO}_2$ .<sup>27</sup> Afonso *et al.* prepared primary amine-modified mesoporous silicas and performed NMR experiments; different conformations of carbamic acid, alkylammonium carbamate as well as hydrogen bonds were confirmed using a density functional theory (DFT) model. The study also provided well understanding of the chemisorbed  $\text{CO}_2$  in amine-oxide hybrid surfaces at a molecular-level.<sup>28</sup>

In this work, PEPA, with similar amino density but a lower price than tetraethylenepentamine (TEPA) and PEI (the price for PEPA, TEPA and PEI were respectively ¥68 per 500 mL, ¥199 per 500 mL and ¥1199 per 500 mL), was impregnated into mesoporous MCM-41 to prepare solid amine sorbents, and MPEG was also codispersed with PEPA to prepare composite sorbents. The pore structures, surface functional groups and desorption properties for MCM-41 before and after loading were characterized; the adsorption and regeneration performances were also studied. In addition, the improvement in the adsorption performance of PEPA-loaded MCM-41 due to the MPEG was also discussed.

## 2. Experimental

### 2.1 Materials

MCM-41 was provided by the Tianjin Nanhua Catalyst Company in China, polyethylene polyamine (PEPA) and methoxypolyethylene glycol (MPEG) were bought from Shanghai Aladdin Bio-Chem Technology Co., Ltd in China, and anhydrous ethanol was supplied by Sinopharm Chemical Reagent Co., Ltd in China.  $\text{N}_2$  (99.999%) and the simulated flue gas, with a volume ratio of 85%  $\text{N}_2$  (99.999%) to 15%  $\text{CO}_2$  (99.999%), were distributed by the Anqiu Hengan Gas Factory.

### 2.2 Preparation of PEPA-loaded MCM-41 before and after MPEG codispersion

The preparation of PEPA-loaded MCM-41 adopted a wet impregnation method under ultrasound-assistance.<sup>15</sup> A calculated volume of PEPA was dissolved in anhydrous ethanol in a beaker, with the solution being sonicated for 30 min; then, MCM-41 with a mass of 1.0 g was quickly added and the beaker was continuously sonicated for another 120 min. The mixture was dried in an electric drying oven at 90 °C for 24 h and named as MCM-41-PEPA $a$ , where  $a$  is the weight loading amount of PEPA in the sorbent.

For PEPA and MPEG codispersed MCM-41, the preparation process was as above, and a calculated amount of PEPA and MPEG were first codispersed in anhydrous ethanol before impregnating into MCM-41. The corresponding composite sorbents were named as MCM-41-PEPA $a$ -Mb, with M representing MPEG and  $a$ ,  $b$  separately representing the weight loading amounts of PEPA, MPEG in the composite sorbents.

### 2.3 Characterization

The  $\text{N}_2$  adsorption-desorption isotherms for PEPA-loaded MCM-41 before and after MPEG codispersion were performed using an ASAP 2460 (Micromeritics, America) at an analysis bath temperature of 77 K. The BET surface area was measured and calculated by the Brunauer–Emmett–Teller (BET) equation; the pore volume was estimated from the  $\text{N}_2$  adsorption amount at a relative pressure of  $P/P_0 = 0.99$ ; the pore size distribution curves were determined from the Barrett–Joyner–Halenda (BJH) desorption branch.

The surface functional groups for PEPA-loaded MCM-41 before and after MPEG codispersion were measured using Fourier-transform infrared spectroscopy (FT-IR) with a TENSOR-27 (Bruker, Germany) over a frequency range of 4000 to 500  $\text{cm}^{-1}$ .

X-ray diffraction patterns were collected using the ASAP 2020 V4.01 X-ray diffractometer with Cu  $\text{K}\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) in the range of  $2\theta = 10 - 80^\circ$ .

Temperature-programmed desorption (TPD) experiments were conducted using a fully automatic multipurpose instrument: a TP-5080 (Xianquan, China).  $\text{CO}_2$  adsorption was performed at 60 °C, and then the temperature was elevated at a rate of 10 K  $\text{min}^{-1}$  in  $\text{N}_2$ .

The thermostability for TEPA and PEPA was determined using a NETZSCH, STA 449F3 (Netzsch, Germany). 10 milligrams of the sample was placed in an alumina pan and  $\text{N}_2$  was passed at a flow rate of 40  $\text{mL min}^{-1}$  at room temperature; then, the temperature was heated to 700 °C at a rate of 10 K  $\text{min}^{-1}$ .

### 2.4 $\text{CO}_2$ adsorption and regeneration experiments

$\text{CO}_2$  adsorption and regeneration experiments were performed on our self-assembled fixed-bed reactor, in which the inner diameter and length of the quartz tube were 0.8 and 40 cm, respectively.<sup>18</sup> The sorbent with a weight of 1.0 g was filled into the reactor, and  $\text{N}_2$  was passed in at a flow rate of 30  $\text{mL min}^{-1}$ ; then, the temperature was increased to 100 °C and held constant for 60 min; the temperature was then decreased to a certain adsorption temperature, and the inlet gas was switched to the simulated flue gas with a flow rate of 30  $\text{mL min}^{-1}$ , where in the  $\text{CO}_2$  adsorption process began. Meanwhile, the  $\text{CO}_2$  concentration at the reactor outlet ( $C$ ) was detected by on-line gas chromatography. When  $C$  doesn't change and equals the  $\text{CO}_2$  concentration at the inlet ( $C_0$ ), an adsorption process finishes, which is called equilibrium adsorption stage, with the adsorption amount at this stage being the equilibrium adsorption capacity; when  $C$  is equal to 5% of  $C_0$ , a breakthrough adsorption stage is reached, in which the adsorption time and amount are called the breakthrough time and breakthrough adsorption capacity. The adsorption capacity was integrally calculated from the breakthrough curve as discussed previously.<sup>15</sup>

After completing the equilibrium adsorption, the inlet gas was switched to  $\text{N}_2$  and the temperature was increased to 100 °C to perform the desorption process. When  $\text{CO}_2$  was not checked at the outlet, the desorption process was completed and the

sorbent was regenerated. Ten adsorption–desorption regenerations were performed in this study.

### 3. Results and discussions

#### 3.1 Characterization

**3.1.1  $N_2$  adsorption–desorption.** The  $N_2$  adsorption–desorption isotherms and pore size distribution curves for MCM-41 before and after loading are shown in Fig. 1, and the BET surface area, total pore volume as well as average pore size are shown in Table 1. As seen in Fig. 1(a), for MCM-41 and MCM-41-PEPA30%, the isotherms suggested a type IV adsorption and hysteric loops suggested a H3 type adsorption, capillary condensation below a relative pressure of 0.4 appeared, showing a mesopore structure for MCM-41 before and after functionalization; for MCM-41-PEPA50% before and after MPEG codispersion, the hysteric loops and capillary condensation phenomenon almost disappeared, showing that most channels were taken up by active components. From Fig. 1(b), the pore size for MCM-41 centered at 2.8 and 3.9 nm, while for MCM-41-PEPA30%, the pores centered at 2.8 nm almost disappeared, suggesting that the active components preferentially

entered relatively small mesopores. As seen from Table 1, the introduction of active components reduced the surface area and pore volume of MCM-41, but for MCM-41-PEPA50% and MCM-41-PEPA50%-M5%, partial pores still remained, which could provide channels for the transfer and capture of  $CO_2$ .

**3.1.2 FT-IR spectra.** The FT-IR spectra for MCM-41 before and after PEPA and MPEG codispersion are shown in Fig. 2. Comparing with MCM-41, MCM-41-PEPA50% showed the bending and symmetric stretching vibrations of N–H from primary amine at 1564 and 1480  $cm^{-1}$ , respectively, the stretching vibrations of C–N from primary or secondary amine at 1230  $cm^{-1}$ , as well as weak stretching vibrations of C–N from tertiary amine at 1317  $cm^{-1}$ , meaning that PEPA was loaded into MCM-41 *via* the wet impregnation method.<sup>15,45</sup> Comparing with MCM-41-PEPA50%, MCM-41-PEPA50%-M5% appeared distinct symmetric and asymmetric stretching vibrations of C–H from the alkyl groups at 2950 and 2840  $cm^{-1}$ , as well as enhanced characteristic peak at 1230  $cm^{-1}$ , which is caused from the asymmetric stretching vibrations of C–O–C in the aliphatic ether or the bending vibrations of C–O–H, suggesting that MPEG was also introduced into MCM-41.<sup>42,45</sup> In addition, the peaks characterizing PEPA all obviously enhanced, which is an indication that MPEG promoted the dispersion and exposure of PEPA in the pore channels of MCM-41.

**3.1.3 Thermostability.** According to previous studies, TEPA-modified mesoporous sorbents suggested good thermostability at a desorption temperature of 100  $^{\circ}C$ .<sup>18,40</sup> The thermal gravimetric curves for PEPA and TEPA were measured under the same conditions and are shown in Fig. 1S in the ESI.† As seen in Fig. 1S,† PEPA and TEPA exhibited almost coincident curves below 140  $^{\circ}C$ , therefore, PEPA-loaded MCM-41 showed a similar thermostability to TEPA-modified MCM-41, which was also thermodynamically suitable for application in adsorption and regeneration processes.

**3.1.4 XRD.** The XRD patterns for MCM-41, MCM-41-PEPA50% and MCM-41-PEPA50%-M5% are shown in Fig. 2S.† MCM-41 appeared a broad peak at  $2\theta = 24.1^{\circ}$ ; for MCM-41-PEPA50% before and after MPEG codispersion, the characteristic peak retained, but suggested a slight shift to the left, showing that the active components were dispersed into the inner surface of MCM-41, and mutual interactions occurred. Similar phenomenon was also reported previously.<sup>15</sup>

#### 3.2 PEPA-loaded MCM-41 for $CO_2$ adsorption

**3.2.1 The effect of the PEPA loading ratio.** Different weight ratios of PEPA-loaded MCM-41 were prepared and studied for  $CO_2$  adsorption at 60  $^{\circ}C$ , and breakthrough adsorption curves along with adsorption capacity data are demonstrated in Fig. 3. As seen in Fig. 3(a), as the PEPA loading was increased, the breakthrough curve shifted towards the right, and the breakthrough time became longer, suggesting improved breakthrough and equilibrium adsorption performance for PEPA-loaded MCM-41 when the PEPA-loading was increased from 30–60%. For MCM-41-PEPA50%, breakthrough time, breakthrough and equilibrium adsorption capacities were 6 min, 1.21 and 1.66  $mmol\ g^{-1}$ , respectively; for MCM-41-PEPA60%, the

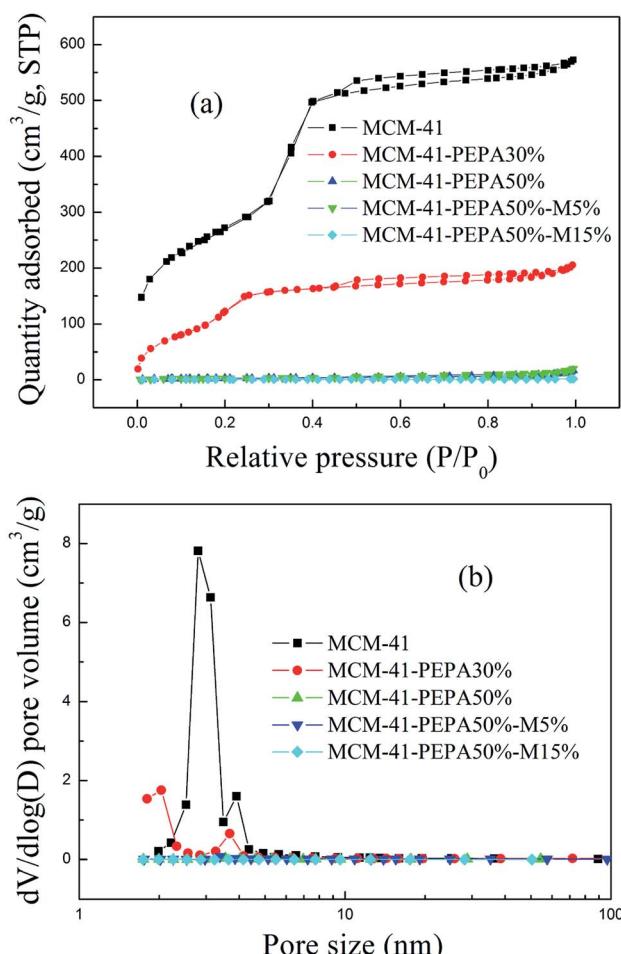


Fig. 1 (a)  $N_2$  adsorption–desorption isotherms and (b) pore size distribution curves for MCM-41 before and after loading.



Table 1 The pore structure data for MCM-41 before and after loading

Sorbent	BET surface area ( $\text{m}^2 \text{ g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \text{ g}^{-1}$ )	Average pore size (nm)
MCM-41	956.15	0.98	3.10
MCM-41-PEPA30%	545.21	0.31	2.30
MCM-41-PEPA50%	10.23	0.023	8.91
MCM-41-PEPA50%-M5%	11.34	0.027	9.68
MCM-41-PEPA50%-M15%	2.33	0.0026	4.39

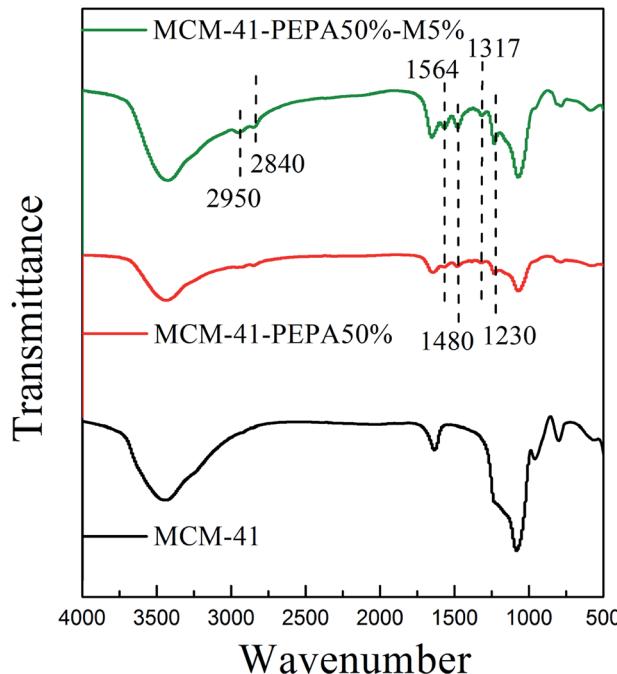


Fig. 2 The FT-IR spectra for MCM-41 before and after PEPA and MPEG codispersion.

corresponding values were 8 min, 1.61 and 1.99  $\text{mmol g}^{-1}$ , respectively, with the adsorption performance being comparable with that of TEPA-modified MCM-41 under the same operating conditions.<sup>42</sup> Accordingly, the PEPA, with also a high amino density but lower price than TEPA, is more suitable for use as a primarily active component for  $\text{CO}_2$  chemisorption.

**3.2.2 The effect of adsorption temperature.** The breakthrough adsorption curves for MCM-41-PEPA50% at 30–80 °C were measured and are shown in Fig. 4(a), with the corresponding breakthrough and equilibrium adsorption capacities being shown in Fig. 4(b). As the temperature was increased, the breakthrough and equilibrium adsorption performance for MCM-41-PEPA50% first increased and then decreased, exhibiting a distinct chemisorption characteristic.<sup>46</sup> High temperature favors not only the dispersal of viscous PEPA in the pore channels of MCM-41 but also  $\text{CO}_2$  flow and collision with exposed active sites, which facilitates  $\text{CO}_2$  adsorption on PEPA-loaded MCM-41.<sup>15,42</sup> However, adsorption is thermodynamically exothermic, and conversely, high temperature hinders  $\text{CO}_2$  adsorption. Therefore, the adsorption performance for PEPA-loaded MCM-41 first increased and then decreased as the

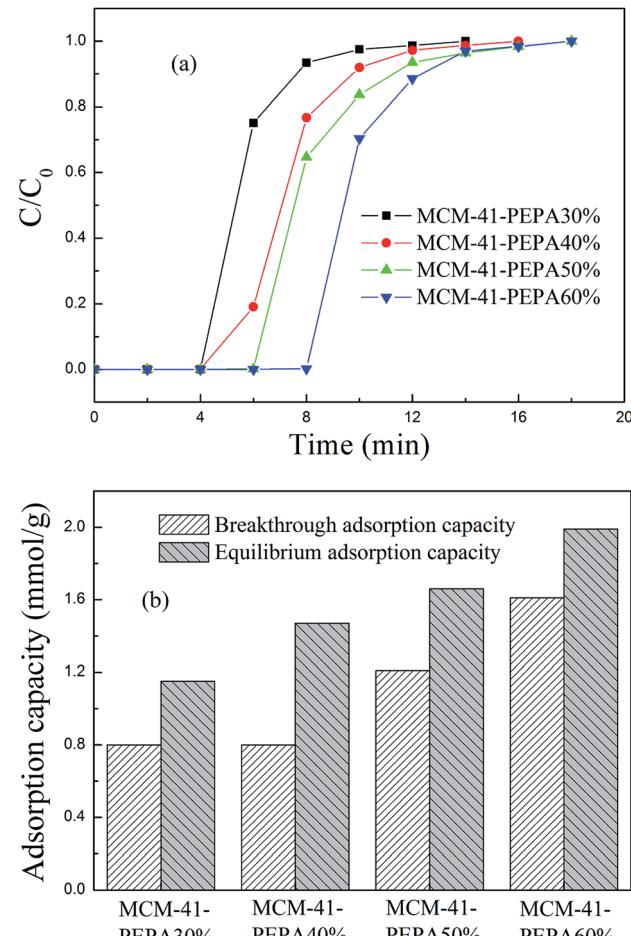


Fig. 3 The (a) breakthrough adsorption curves and (b) adsorption capacities for PEPA-loaded MCM-41 at 60 °C.

temperature was increased; the optimal adsorption temperature, breakthrough and equilibrium adsorption capacity were 60 °C, 1.21 and 1.66  $\text{mmol g}^{-1}$ , respectively.

### 3.3 PEPA and MPEG codispersed MCM-41 for $\text{CO}_2$ adsorption

**3.3.1 The effect of the MPEG mass ratio on PEPA.** Different mass ratios of PEPA and MPEG were codispersed in MCM-41 to discuss the effect of MPEG on the adsorption performance of PEPA-loaded MCM-41 at 60 °C, with the breakthrough adsorption curves and adsorption capacities demonstrated in Fig. 5–7. For MCM-41-PEPA30%, MCM-41-PEPA40% and MCM-41-



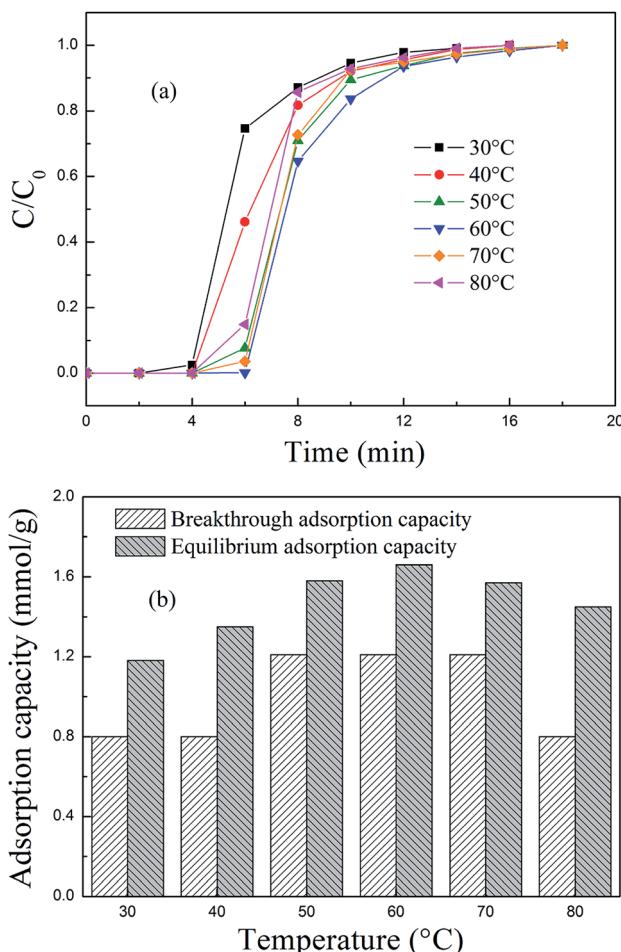


Fig. 4 The (a) breakthrough adsorption curves and (b) adsorption capacities for MCM-41-PEPA50% at different adsorption temperatures.

PEPA50%, the introduction of MPEG caused all breakthrough curves to move towards the right, and breakthrough and equilibrium adsorption performance increased. For MCM-41-PEPA30%-M20%, the breakthrough and equilibrium adsorption capacities were respectively 1.21 and 1.97 mmol g<sup>-1</sup>, which were improved by 51% and 71% compared to the corresponding values for MCM-41-PEPA30%; for MCM-41-PEPA40%-M10%, the breakthrough and equilibrium adsorption capacities were respectively 1.61 and 2.22 mmol g<sup>-1</sup>, which were improved by 101% and 51% compared to the corresponding values for MCM-41-PEPA40%; for MCM-41-PEPA50%-M5%, the breakthrough and equilibrium adsorption capacities were respectively 1.61 and 2.25 mmol g<sup>-1</sup>, which were improved by 37% and 40% compared to the corresponding values for MCM-41-PEPA50%. To sum up, the codispersion of MPEG improved the adsorption performance for PEPA-loaded MCM-41, which might be caused by the hydrogen bonding interactions between the ether groups and hydroxyl groups from MPEG with the amino groups from PEPA, and similar phenomenon has also been reported.<sup>41,43</sup> The hydrogen bonding interactions are expressed as follows.

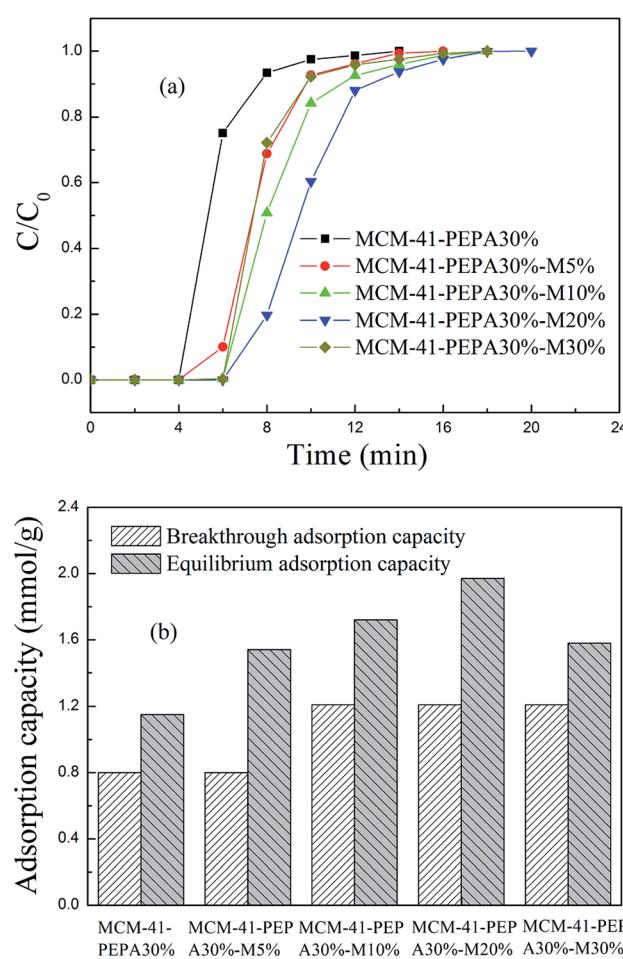
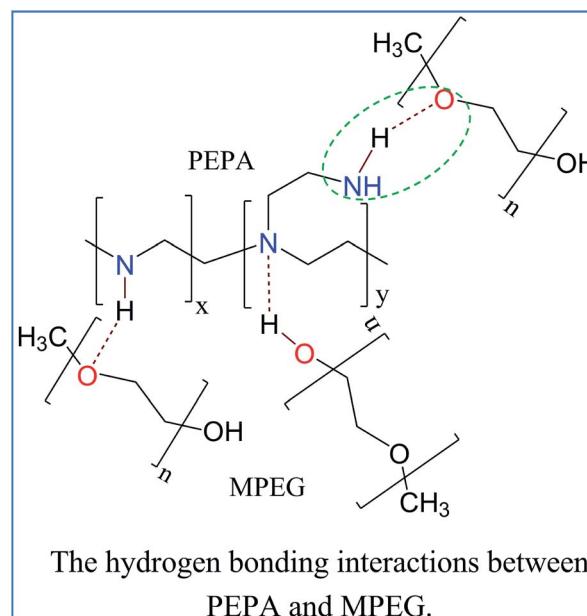


Fig. 5 The (a) breakthrough adsorption curves and (b) adsorption capacities for 30 wt% PEPA and different ratios of MPEG codispersed MCM-41 at 60 °C.



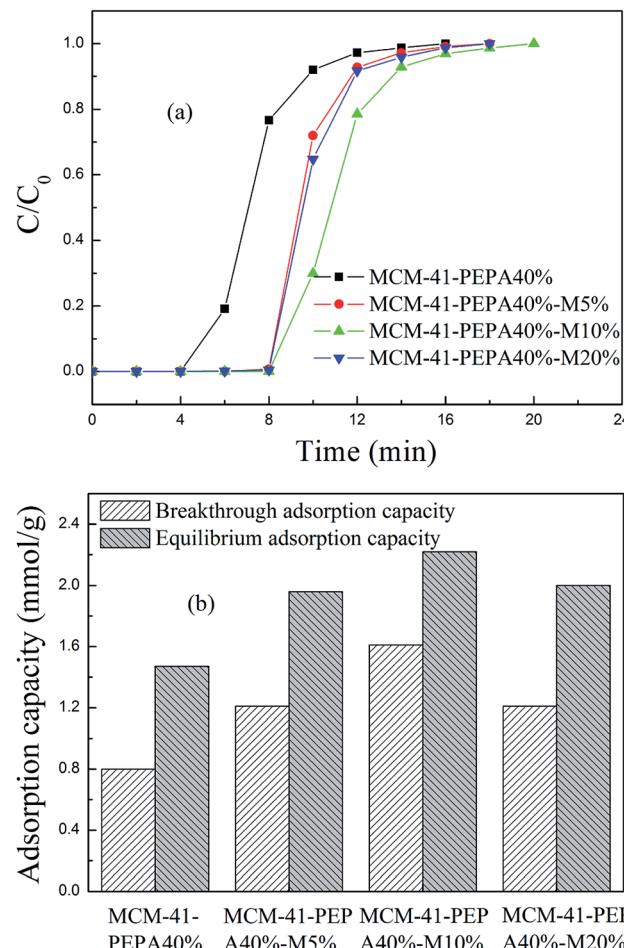


Fig. 6 The (a) breakthrough adsorption curves and (b) adsorption capacities for 40 wt% PEPA and different ratios of MPEG codispersed MCM-41 at 60 °C.

However, the increasing of MPEG didn't cause the adsorption performance for PEPA-loaded MCM-41 to improve continuously, but showed a gradual reduction. MPEG improved the dispersion of easily agglomerated PEPA into the pore channels of MCM-41, but too much MPEG addition could also lead to channel blockage and a decrease in adsorption performance. Among the studied sorbents, 50 wt% PEPA and 5 wt% MPEG codispersed MCM-41 showed good adsorption performance at 60 °C.

**3.3.2 The effect of adsorption temperature.** Considering the good adsorption performance at 60 °C, the breakthrough curves and adsorption capacities for MCM-41-PEPA50%-MPEG5% at different temperatures were investigated and are shown in Fig. 8. As the temperature was increased, the breakthrough curve first moved towards the right and then the left; so, the corresponding breakthrough and equilibrium adsorption capacities first increased and then decreased, which is also a distinct chemisorption characteristic. The optimum adsorption performance for MCM-41-PEPA50%-M5% appeared at 50 °C, which is lower than that of MCM-41-PEPA50%. The possible explanation for this was that the hydrogen bonding

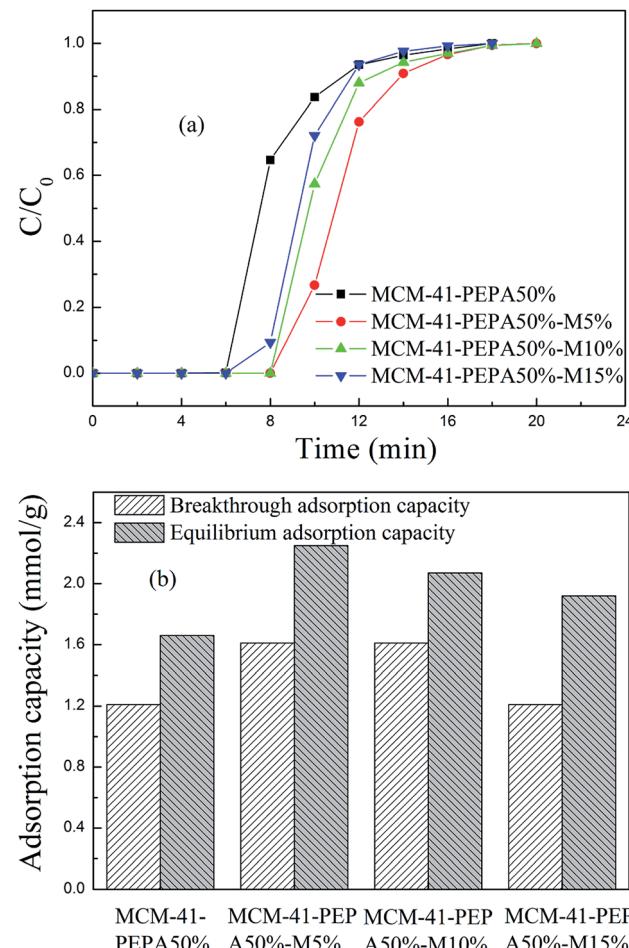


Fig. 7 The (a) breakthrough adsorption curves and (b) adsorption capacities for 50 wt% PEPA and different ratios of MPEG codispersed MCM-41 at 60 °C.

interactions between PEPA and MPEG improved the dispersion and exposure of active amino groups, so the optimal adsorption temperature decreased to a more thermodynamic point. At 50 °C, the breakthrough and equilibrium adsorption capacity for MCM-41-PEPA50%-M5% was 2.01 and 2.39 mmol g<sup>-1</sup>, respectively, which was increased by 66% and 51% compared to the corresponding values for MCM-41-PEPA50%.

### 3.4 Regeneration

MCM-41-PEPA50% and MCM-41-PEPA50%-M5% were selected to further investigate the regenerability during 10 adsorption-desorption cycles. The adsorption temperatures for MCM-41-PEPA50% and MCM-41-PEPA50%-M5% were respectively 60 and 50 °C, and the desorption temperatures were all 100 °C, which were set according to previous studies.<sup>40</sup> The equilibrium adsorption capacity data *versus* cycle number figures are depicted in Fig. 9. For both sorbents, the adsorption capacity remained stable during the first three cycles, and then showed a slight decrease. After 10 regenerations, the equilibrium adsorption capacity for MCM-41-PEPA50%-M5% was reduced by 5.0% compared to the fresh sorbent, being better than the

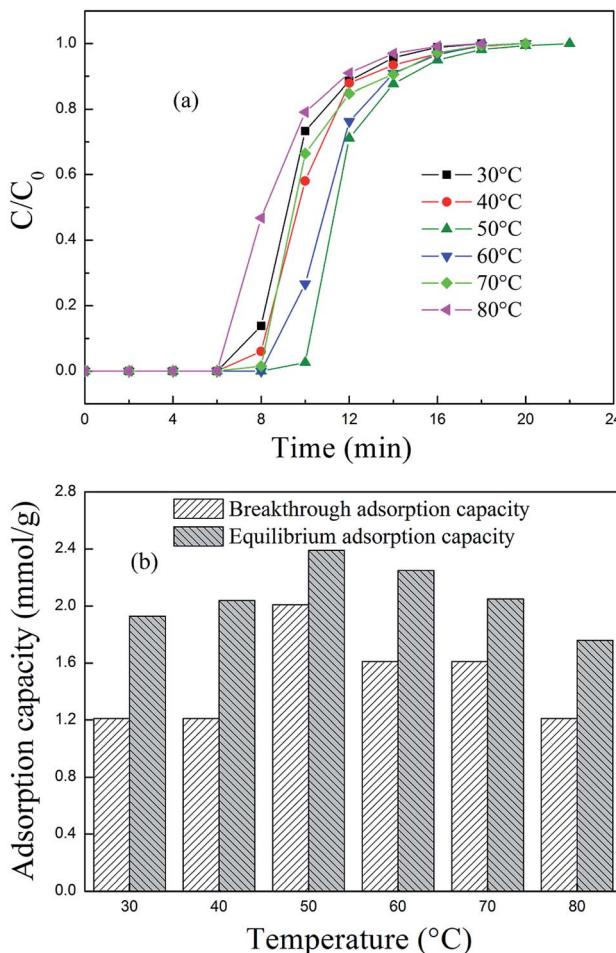


Fig. 8 The (a) breakthrough adsorption curves and (b) adsorption capacities for MCM-41-PEPA50%-M5% at different adsorption temperatures.

corresponding value of 7.8% for MCM-41-PEPA50%. Thus, the introduction of MPEG improved the regenerability for PEPA-loaded MCM-41; the reason for this was attributed to the synergistic interactions between functional groups. The synergistic interactions enhanced the stability of PEPA in MCM-41, which reduced its loss during regenerations.

The FT-IR and XRD spectra for MCM-41-PEPA50%-M5% before and after 10 cycles are shown in Fig. 3S and 4S.† Comparing with fresh MCM-41-PEPA50%-M5%, the characteristic peaks for the regenerated sample still retained, suggesting a good regenerability of MCM-41-PEPA50%-M5%; but the peak intensity showed slight decrease, which was due to the evaporation or degradation of the active composites during regenerations. The phenomenon was in accordance with the results from Fig. 9.

### 3.5 Adsorption and desorption kinetics

**3.5.1 Adsorption kinetics.** The adsorption rate curves for MCM-41-PEPA50% at 60 °C and MCM-41-PEPA50%-M5% at 50 °C are shown in Fig. 10(a). For both sorbents, the rate curves

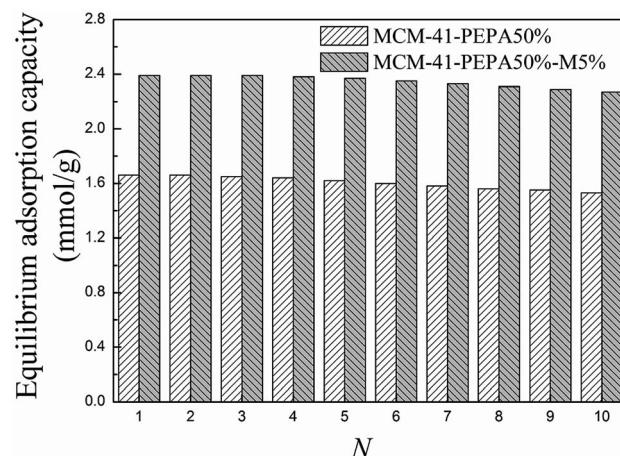


Fig. 9 The equilibrium adsorption capacities for MCM-41-PEPA50% and MCM-41-PEPA50%-M5% during 10 adsorption–desorption cycles.

showed two stages, with a rapid adsorption stage following a relatively slow stage; the point corresponding to the breakthrough adsorption time was determined to be the boundary point of two stages. The rapid stage corresponds to the breakthrough adsorption process, with the rate being  $0.20 \text{ mmol g}^{-1} \text{ min}^{-1}$ ; for MCM-41-PEPA50%, the adsorption capacity in the rapid stage was  $1.21 \text{ mmol g}^{-1}$ , accounting for 73% of the equilibrium adsorption capacity, while for MCM-41-PEPA50%-M5%, the adsorption capacity in the rapid stage was  $2.01 \text{ mmol g}^{-1}$ , accounting for 84% of the equilibrium adsorption capacity, with this value being much higher than that obtained for MCM-41-PEPA50%. In view of the adsorption efficiency, the sorbents are usually regenerated after completing the breakthrough stage. Therefore, the addition of MPEG improved the adsorption efficiency and kinetics for PEPA-loaded MCM-41.

**3.5.2 Temperature programmed desorption (TPD) experiments.** The TPD curves for MCM-41-PEPA50% and MCM-41-PEPA50%-M5% are shown in Fig. 10(b). In MCM-41-PEPA50%, a weak desorption peak at 80 °C and a strong desorption peak at 117 °C appeared, which corresponded to physisorbed and chemisorbed  $\text{CO}_2$ , respectively; there is only one kind of basic site in PEPA-loaded MCM-41: the amino groups from PEPA.

In MCM-41-PEPA50%-M5%, two strong desorption peaks appeared at both 80 and 117 °C, suggesting that the addition of MPEG changed the basic sites in the sorbents. In addition to the original amino sites from PEPA, other basic sites appeared at a much lower temperature of 80 °C, which were the amino groups participating in the hydrogen bonding interactions with the ether and hydroxyl groups from MPEG. The hydrogen bonding interactions helped with the dispersion and exposure of the amino groups, and the optimum adsorption temperature for codispersed MCM-41 was reduced to 50 °C. The  $\text{CO}_2$ -TPD results also confirmed the mutual interactions between PEPA and MPEG, with similar phenomenon previously reported for  $\text{NaNO}_3$ -promoted  $\text{MgO}$  for  $\text{CO}_2$  capture.<sup>47</sup>



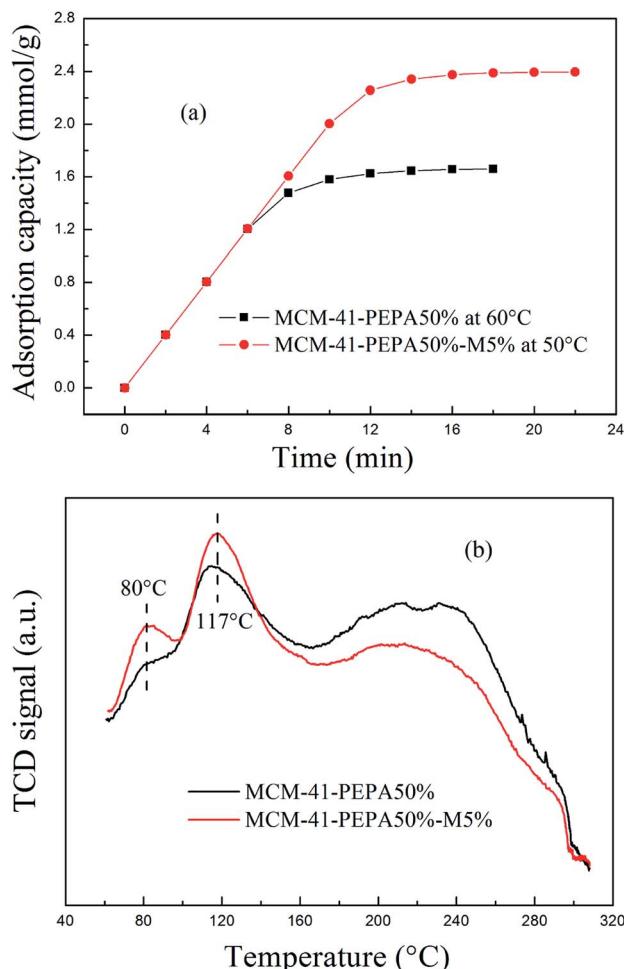


Fig. 10 The (a) adsorption rate curves and (b) TPD curves for MCM-41-PEPA50% and MCM-41-PEPA50%-M5%.

## 4. Conclusions

PEPA, with a similar amino density but lower price than TEPA, was found to be more suitable for preparing amine-loaded MCM-41 sorbents, in which the breakthrough and equilibrium adsorption performance as well as regenerability were found to be comparable with that for TEPA-loaded MCM-41. To improve the exposure and dispersion of viscous PEPA in MCM-41, different mass ratios of MPEG were codispersed and coimpregnated into MCM-41 to prepare composite sorbents for CO<sub>2</sub> capture. For 50 wt% PEPA and 5 wt% MPEG codispersed MCM-41, the breakthrough and equilibrium adsorption capacities were respectively 2.01 and 2.39 mmol g<sup>-1</sup> at 50 °C, which were improved by 66% and 44% compared to the corresponding values for 50 wt% PEPA-loaded MCM-41 under the same operating conditions; after 10 regenerations, the equilibrium adsorption capacity was reduced by 5.0%, which is lower than the corresponding value of 7.8% for 60 wt% PEPA-loaded MCM-41.

The codispersed sorbent of MCM-41-PEPA50%-M5% showed a rapid breakthrough adsorption stage, with a rate of 0.20 mmol g<sup>-1</sup> min<sup>-1</sup>, and showed an adsorption capacity that was 84% of

the equilibrium adsorption capacity, indicating a high adsorption efficiency. The CO<sub>2</sub>-TPD results indicated that the codispersed MCM-41 contained two kinds of basic sites, with one appearing at a lower temperature, which was attributed to the synergistic hydrogen bonding interactions between PEPA and MPEG.

## Conflicts of interest

There are no conflicts to declare.

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