Adsorption of carbon dioxide by a novel amine impregnated ZSM-5/KIT-6 composite

Zhifeng Lin, Jianwen Wei, Linlin Geng, Dejun Mei and Lei Liao

A novel amine modified composite was fabricated for CO2 capture. Tetraethylpentamine (TEPA) or polyethyleneimine (PEI) was selected to modify the micro/mesoporous ZSM-5/KIT-6 composite (ZK).

1. Introduction

The continuous increase in emissions of CO2 mainly derived from burning a great deal of fossil fuels is aggravating climate change and global warning.1-2 The reduction of CO2 emissions is imperative for the mitigation of global warming for which capture of CO2 from flue gas is an effective method. Recently, many kinds of CO2 capture technologies have been developed to reduce CO2 emissions.3-4 Chemical absorption with amines has been commercialized on a large scale,5-7 but there are many adverse effects, such as wastage of solvent due to amine volatilization, demand of high energy and generation of waste during regeneration and limitation of operational lifetime due to solvent degradation.8-10 However, adsorption with porous solids has advantages, such as friendliness to the environment and long operational lifetime.11-12 Therefore, there have been various porous materials designed as adsorbents for use in CO2 capture, such as zeolites,13-15 mesoporous silicas,14,15 metal organic frameworks,16-18 and activated carbons.19,20

Zeolites, a class of crystals with regular hole wall, such as ZSM-5, 13X, β, and 5A, have been widely used in industrial applications due to their excellent adsorption capacities at low CO2 partial pressure and high reusability in regeneration. With medium pore size and abundant microporous structure, zeolite ZSM-5 is efficient for CO2 capture through physisorption formed by van der Waals’ force or hydrogen bonding. Hefti et al. found that the CO2 uptake of ZSM-5 was 1.35 mmol g⁻¹ at 25 °C and CO2 partial pressure of 100 kPa and a higher value of 2.34 mmol g⁻¹ was obtained as increasing pressure to 1000 kPa.21 Mesoporous silicas, a class of silica-based inorganic materials with amorphous pore wall, such as KIT-6, SBA-15, MCM-48 and MCM-41, have been widely investigated due to high pore volume and surface area. With abundant mesoporous structure and large pore size, silica-based KIT-6 is beneficial to accommodate more amines to react with CO2 for chemisorption. As a result, KIT-6 has demonstrated a better CO2 adsorption performance over many other silica-based materials after impregnation with polyethyleneimine (PEI) as previously reported by Son et al.22 At 75 °C and CO2 partial pressure of 101 kPa, an maximum uptake of 3.07 mmol g⁻¹ was found for PEI-loaded KIT-6.23 The composites combined with zeolites and mesoporous silicas have common advantages, which are the optional adsorbents. Santos et al. fabricated micro/mesoporous composites containing zeolite ZSM-12 and mesoporous silica MCM-41 via the self-assembly procedure.24 At 25 °C and CO2 partial pressure of 101 kPa, the composite ZSM-12/MCM-41 displayed a better capacity (0.94 mmol g⁻¹) than those of ZSM-12 (0.86 mmol g⁻¹) and MCM-41 (0.27 mmol g⁻¹), which is attributed to the synergistic effect. What’s more, further improvement in the adsorption performance may be achieved after amine modification.

Inserting alkaline amine groups into adsorbents can improve CO2 chemisorption, which can be normally achieved in three routes: amines anchored to the supports in the form of covalent bonds,25 amines impregnated into the inner channel of supports26,27 and amine containing polymers introduced directly without second modification by molecular imprinting technology.28,29 In the first route, the grafted amines are usually aminosilanes. For instance, (3-aminopropyl) triethoxysilane

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(APTES) was well grafted onto the surface of KIT-6 in dry solution, presenting a uptake of 0.9 mmol g⁻¹ at CO₂ partial pressure of 100 kPa and 30 °C as reported by Kishor et al.¹⁹ In the second route, PEI and tetraethylenepentamine (TEPA) are the usual modifying reagents. For example, PEI was impregnated into the inner channel of composite 5A@mesoporous silica fabricated via the sol–gel coating procedure as reported by Liu et al.¹³ Besides, the amine containing polymers can also be used as grafted or impregnated amines. For example, the silica gel was grafted or impregnated with acrylamide polymer as reported by Zhao et al.¹² In the last route, the molecularly imprinted CO₂ adsorbents were developed by Zhao et al., using ethanedioic acid as template, acrylamide as functional monomer and ethylene glycol dimethacrylate as cross-linker.²⁸,²⁹ Inspired by these reports, the composite support with amine loading would be a feasible strategy for designing amine modified solid composite.

Up to now, amine modified composites for CO₂ capture are rarely reported. Herein, an amine impregnated composite strategy was used to fabricate the two series of adsorbents, TEPA-loaded ZSM-5/KIT-6 and PEI-loaded ZSM-5/KIT-6. At the same time, it was found that there are many superiorities in amine impregnated ZSM-5/KIT-6 over the conventional silica-based materials, including high amine loading, high CO₂ adsorption capacity, high amine efficiency, rapid kinetics, high enthalpy and high regeneration performance.

2. Experimental

2.1. Preparation of support and amine loaded samples

ZSM-5/KIT-6 (Si/Al = 50) with molar composition of 1 TEOS:0.02 Al:0.017 P123:1.32 BuOH:195 H₂O:1.83 HCl was prepared through an assembly procedure.³³ First, 8.5 g of tetraethyl orthosilicate (TEOS, 99 wt%, Aldrich) was gradually dropped into the mixture of 16.87 g of distilled water, 4.54 g of tetraethyl ammonium hydroxide solution (TEAOH, 25 wt%, Acros Organics) and 0.167 g of aluminium isopropoxide (AIP, 99.99 wt%, Acros Organics) with vigorous stirring at 35 °C for 2 h. Then, hydrothermal treatment was performed at 150 °C for 10 h, giving resultant sample ZSM-5 S₁. Second, 4 g of n-butanol (BuOH, 99.5 wt%, Sinopharm Chem. Reagent Co.) was added into P123 solution containing 4 g of P123 (EO₂₀PO₇₀EO₂₀, M_w = 5800, Aldrich), 125 g of distilled water and 7.5 g of HCl (36 wt%, Xilong Chem. Reagent Co.). The mixture was stirred at 35 °C for 1 h, giving it S₂. Third, as cooling to room temperature, S₁ was uniformly added to S₂, and then stirred at 35 °C for 24 h before the hydrothermal process was performed at 100 °C for 24 h. As cooling to room temperature, the product was filtered, dried at 100 °C for 24 h and calcined at 550 °C for 6 h with a heating rate of 5 °C min⁻¹. The as-synthesized composite is denoted as ZK.

Inspired by these reports, the composite support with amine loading would be a feasible strategy for designing amine modified solid composite. TEPA or PEI was introduced into the ZK support by wet impregnation. The typical impregnation step carried out at atmospheric pressure was depicted as follows. A certain amount of TEPA or PEI was dispersed in 25 ml ethanol (Xilong Chem. Reagent Co.) under stirring for 30 min at room temperature. Subsequently, 0.5 g of ZK support was added under further stirring for 6.5 h. The ethanol was evaporated and the mixture was dried at 80 °C in air for 16 h. The samples are referred to ZK-TEPA-X or ZK-PEI-X (X = 50, 60, 70 or 80), where X stands for mass fraction of TEPA or PEI. For instance, ZK-TEPA-60 indicates that the ZK is loaded with 60% TEPA.

A schematic representation of the process for the preparation of ZK-TEPA-X or ZK-TEPA-X is shown in Fig. 1.

2.2. Characterization

Thermal gravimetric and derivative thermogravimetric analysis (TGA/DTG) was performed on a SDT Q600 TGA (TA, USA) in nitrogen flow up to 800 °C.

Elemental analysis was carried out with a EA 2400 II elemental analyzer (Perkin-Elmer, USA) for nitrogen content of various samples.

Fourier transform infrared spectra (FTIR) were detected with a Nexus 470 IR spectrometer (Nicolet, USA) in wavenumber range of 4000–400 cm⁻¹. Detected wafers were made by mixing the samples and KBr with a mass ratio of 1 : 100.

**Fig. 1** Schematic representation of the preparation of ZK-TEPA-X.
Nitrogen adsorption/desorption tests were carried out at 
−196 °C with a NOVA2000e automatic surface analyzer (Quan-
tachrome, USA). Each sample was outgassed at 100 °C in 
nitrogen atmosphere for 8 h before test. The surface area was 
calculated by Brunauer–Emmett–Teller (BET). Total pore 
volume was calculated from N$_2$ adsorption capacity at $P/P_0 = 
0.99$.

2.3. CO$_2$ adsorption

CO$_2$ adsorption capacity was determined by SDT Q600 TGA (TA, 
USA) with a scale of 0.1 μg. In a typical experiment, a certain 
amount of sample was put in a 0.05 cm$^3$ platinum pan and 
regenerated (heated up to 110 °C with a heating rate of 
10 °C min$^{-1}$ and kept at 110 °C to get a constant weight) in N$_2$ 
(100 cm$^3$ min$^{-1}$) prior to adsorption. Then the sample was 
cooled to 60 °C before exposure to the CO$_2$/N$_2$ mixed gases 
(15 vol% CO$_2$) until the quantity of sample displayed no 
noticeable changes. The weight change and heat 
enthalpy was calculated from the heat 
flow versus time and dry 
mass of sample according to the following equation (eqn (1)) and 
dry equilibrium 
(2):

$$q_e = \frac{(m_c - m_d)/44.01}{m_d/1000}$$  \hspace{1cm} (1)

$$H_{ads} = \frac{44.01 \phi t}{1000 m_d}$$  \hspace{1cm} (2)

where $q_e$ is the equilibrium adsorption capacity of CO$_2$ 
(mmol g$^{-1}$), $m_c$ and $m_d$ are the sample weights after equilibrium 
and dehydration (mg), respectively, $H_{ads}$ is the enthalpy (kJ mol$^{-1}$), 
$\phi$ is the heat flow (mW), $t$ is the time versus heat flow (s).

The CO$_2$ saturated sample was regenerated in the same proce-
dure as described above before adsorption was carried out at 60 °C. 
Thus, the cyclic performance during five recycles was explored.

3. Results and discussion

3.1. Characterization

TGA weight loss curves of ZK loaded with various amounts of 
TEPA and PEI are shown in Fig. 2a, and the corresponding DTG 
curves are shown in Fig. 2b. All samples exhibited original 
weight losses below 120 °C due to liberation of moisture and 
CO$_2$. The further remarkable weight loss emerged in the range 
of 125–400 °C for samples of TEPA-loaded ZK, and 190–400 °C 
for samples of PEI-loaded ZK. ZK-TEPA-50 displayed an 
maximum weight loss rate at 217 °C while 303 °C for ZK-PEI-50, 
which can be associated with the decomposition of TEPA and 
PEI, respectively. With the increase of the amine loadings, the 
sharp weight loss peak shifted slightly towards the higher 
temperature for both TEPA-loaded and PEI-loaded samples. The 
introduction of more TEPA or PEI into the nanoporous support 
increased the particle size of the sample, resulting in the 
increase of decomposition temperature.\textsuperscript{25} Besides, higher 
decomposition temperatures for PEI-loaded samples than 
TEPA-loaded samples indicated that the thermal stability was 
enhanced as the amine molecular weight increased. In this 
stage, the weight losses of about 45.3%, 57.53%, 67.42% and 
72.99% were obtained for ZK-TEPA-50, ZK-TEPA-60, ZK-TEPA-70 
and ZK-TEPA-80, respectively. The actual amine contents were 
very close to the theoretical values, indicating that TEPA was 
loaded well onto the support during the impregnation process. 
While ZK-PEI-50, ZK-PEI-60, ZK-PEI-70 and ZK-PEI-80 showed 
the smaller weight losses of about 39.23%, 51.25%, 63.49% and 
76.71%, respectively. It can be ascribed to the larger amine 
with large molecular size and viscosity of PEI. PEI with large molecular 
size is not easy to enter the support and its large viscosity made 
the agglomeration occur more easily. As temperature exceeded 
400 °C, there was no obvious weight loss and the different 
remaining weights were observed at 800 °C. It was due to the 
high heat resistant silica existing in the molecular sieve 
framework. ZK loaded with TEPA and PEI displayed thermal 
stability in N$_2$ up to 125 and 190 °C, respectively, which indicated 
that the regeneration temperature of 110 °C was suitable for the cyclic adsorption/desorption on all the samples.

The amount of amine groups impregnated in the ZK can also 
be determined by elemental analysis. Nitrogen contents in ZK 
modified with TEPA or PEI are listed in Table 1. When amine 
loading increased from 50 to 80%, the nitrogen contents 
increased from 12.06 to 20.46 mmol g$^{-1}$ for TEPA-loaded 
samples, while 9.54 to 17.66 mmol g$^{-1}$ for PEI-loaded 
samples, which were in close agreement with TGA results.

![Fig. 2](image-url) (A) TGA curves and (B) DTG curves of (a) ZK-TEPA-50, (b) ZK-TEPA-60, (c) ZK-TEPA-70, (d) ZK-TEPA-80, (e) ZK-PEI-50, (f) ZK-PEI-60, (g) ZK-PEI-70 and (h) ZK-PEI-80.
### Table 1

<table>
<thead>
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<th>Adsorbent</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{total}}$ (cm$^3$ g$^{-1}$)</th>
<th>Nitrogen content (mmol g$^{-1}$)</th>
<th>Capacity (mmol g$^{-1}$)</th>
<th>Amine efficiency (mmol CO$_2$/mmol N)</th>
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<td>—</td>
<td>20.46</td>
<td>4.76</td>
<td>0.23</td>
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</tbody>
</table>

The FTIR spectra of ZK support, TEPA-loaded ZK and PEI-loaded ZK are shown in Fig. 3. The characteristic bands of KIT-6 around 1096, 802 and 459 cm$^{-1}$ were identified over all the samples due to Si–O–Si asymmetric, symmetric stretching and bending vibrations, respectively. While the band at 544 cm$^{-1}$ associated with typical vibration modes of ZSM-5 (five-membered rings of T–O–T, T = Si or Al) in ZK shifted slightly towards the higher wavenumbers as shown in the spectra of ZK-TEPA-60 and ZK-PEI-60. The bands at 3467, 1638 and 967 cm$^{-1}$ were associated with O–H stretching vibration of silanol groups, H–O–H bend, and Si–O stretching vibration of free silanol groups, respectively. After TEPA or PEI impregnation, these bands either got weakened or eliminated entirely, which indicated that a part amount of amine groups in TEPA or PEI can interact with free silanol groups in ZK. The relevant reaction equations are given as follows:

$$\text{Si–OH} + \text{RNH}_2 \rightarrow \text{Si–O}^+ \text{N}^- \text{H}_3\text{R}$$  \hspace{1cm} (3)

$$\text{Si–OH} + \text{R}_2\text{NH} \rightarrow \text{Si–O}^+ \text{N}^+ \text{H}_3\text{R}_2$$  \hspace{1cm} (4)

Besides the elimination of the band of free silanol groups, some new bands around 2956, 2854, 1634, 1573, 1481 and 1320 cm$^{-1}$ appeared after TEPA or PEI loading in ZK. The bands around 2956 and 2854 cm$^{-1}$ were associated with C–H asymmetric and symmetric stretching vibrations, while the band around 1481 cm$^{-1}$ was associated with C–H deformation. A weak band around 1634 cm$^{-1}$ was found, related to N–H deformation of protonated primary amine groups (Si–O–N–H$_3$R) or secondary amine groups (Si–O–N–H$_3$R$_2$) formed through reactions in eqn (3) and (4). The bands around 1573 and 1319 cm$^{-1}$ were respectively associated with N–H deformation of primary amine groups and C–N stretching vibration. The spectra of ZK-TEPA-60 and ZK-PEI-60 after CO$_2$ adsorption are also included in Fig. 3. A new band at 1415 cm$^{-1}$ was identified in both spectra, attributed to NCOO skeletal vibration of carbamate formed from the reactions between amine groups and CO$_2$ molecules. These reactions that may occur during CO$_2$ adsorption process are depicted as follows:

$$\text{CO}_2 + 2\text{R}_1\text{NH} \rightarrow \text{RNHCOO}^- + \text{RNH}_3^+$$  \hspace{1cm} (5)

$$\text{CO}_2 + 2\text{R}_1\text{R}_2\text{NH} \rightarrow \text{R}_1\text{R}_2\text{NCOO}^- + \text{R}_1\text{R}_2\text{NH}_2^+$$  \hspace{1cm} (6)

$$\text{CO}_2 + \text{R}_2\text{NH} + \text{RNH}_2 \rightarrow \text{R}_2\text{NCOO}^- + \text{RNH}_3^+ \text{ (or RNHCOO}^- + \text{R}_2\text{NH}_2^+)$$  \hspace{1cm} (7)

The N$_2$ adsorption/desorption isotherms of TEPA-loaded ZK and PEI-loaded ZK belonging to type IV isotherms are shown in Fig. 4, while the textural properties such as specific surface area ($S_{\text{BET}}$) and total pore volume ($V_{\text{total}}$) were listed in Table 1. When amine loading increased from 50 to 70%, the value of $S_{\text{BET}}$ decreased from 73.2 to 9.7 m$^2$ g$^{-1}$ for PEI-loaded samples, while 94.3 to 30.8 m$^2$ g$^{-1}$ for TEPA-loaded samples. Similarly, the value of $V_{\text{total}}$ decreased from 0.20 to 0.03 cm$^3$ g$^{-1}$ for PEI-loaded samples, while 0.25 to 0.07 cm$^3$ g$^{-1}$ for TEPA-loaded samples.

#### 3.2. CO$_2$ adsorption

The CO$_2$ adsorption curves of ZK loaded with various amounts of TEPA and PEI with an adsorption temperature of 60 °C are shown in Fig. 5a and b, respectively. The adsorption data is given in Table 1. When amine loading was 50%, ZK-TEPA-50 demonstrated an appreciable adsorption capacity of 4.27 mmol g$^{-1}$, whereas ZK-PEI-50 demonstrated that of 3.24 mmol g$^{-1}$. The maximum values in the two series were 5.32 and 4.49 mmol g$^{-1}$ for ZK-TEPA-60 and ZK-PEI-60, respectively. The increase of adsorption capacity was due to the increased nitrogen content and the enhanced chemisorption between amine groups and CO$_2$ (Table 1, Fig. 5). Despite the reduction of physisorption due to the decrease of surface area and pore volume, the enhanced chemisorption due to the increase of nitrogen content may be dominant in the CO$_2$ adsorption,
resulting in the increase of adsorption capacity (Table 1, Fig. 5). Increasing amine loading to 70%, the capacity decreased to 4.85 mmol g\(^{-1}\) for ZK-TEPA-70 and 3.93 mmol g\(^{-1}\) for ZK-PEI-70. Further increasing amine loading to 80%, the value decreased to 4.76 mmol g\(^{-1}\) for ZK-TEPA-80, but ZK-PEI-80 demonstrated an apparent decrease in uptake of 2.91 mmol g\(^{-1}\). Mesoporous structure of KIT-6 in the composites offered large space and channel for the loading of amine groups as well as CO\(_2\) diffusion and the microporous structure of ZSM-5 in the composites played a major role in physisorption of CO\(_2\). Although the nitrogen contents in the two series increased significantly as amine loadings were increased to 70%, this property could not compensate for the great losses of surface area as well as pore volume (Table 1). The high loading of amines blocked the ZSM-5 pores and limited the diffusion of CO\(_2\) to ZSM-5 channels and to the active adsorption sites on amine groups, resulting in the lower adsorption capacities compared to the maximum values.

On the other hand, TEPA-loaded samples displayed higher CO\(_2\) adsorption capacities compared to those of corresponding PEI-loaded samples. For ZK-TEPA-X, TEPA was well dispersed in the inner channels of composites even at high loading of 60% while retaining a pore volume of 0.09 cm\(^3\) g\(^{-1}\) as well as a surface area of 40.9 m\(^2\) g\(^{-1}\), because of its low molecular weight and linear properties (Table 1). These common effects were beneficial to the improvement of adsorption capacity due to the easiness for CO\(_2\) to overcome the diffusion resistance and access to the active sites. For ZK-PEI-X, due to the high molecular weight and polymeric properties of PEI, the dispersion of PEI in composites was low and the significant losses of pore volume and surface area were found (Table 1). These effects caused damage to the accessibility of PEI and resulted in the lower adsorption capacities compared to those of ZK-TEPA-X. It can be concluded that the amine content (nitrogen content) and the accessibility of active sites on amine groups to interact with CO\(_2\) are the important factors for the efficient use of an adsorbent in CO\(_2\) capture.

In addition, the amine efficiency of the adsorbents calculated from the ratio between CO\(_2\) capture capacity and nitrogen content are given in Table 1. CO\(_2\) adsorption capacity and amine efficiency with amine loading for ZK-TEPA-X and ZK-PEI-X are shown in Fig. 6a and b, respectively. The reaction between CO\(_2\)
and amine groups needs two amine groups per CO$_2$ molecule (eqn (4)–(6)), so the amine efficiency should not exceed 0.5 normally.** The similar trends were observed in both series. The amine efficiency increased first and then decreased with the increase of amine loadings. ZK-TEPA-60 displayed an maximum amine efficiency of 0.38, which was higher than that of ZK-PEI-60 (0.35).

The adsorption temperature is an important factor for chemisorption of CO$_2$, so the effects of various temperatures (30, 45, 60, 75 and 90 °C) on adsorption capacities of ZK-TEPA-60 and ZK-PEI-60 were investigated as shown in Fig. 7a and b, respectively. For ZK-TEPA-60, the adsorption capacity increased in the temperature range of 30–60 °C while decreased in range of 60–90 °C. The similar trend was observed for ZK-PEI-60 while the optimum temperature of ZK-PEI-60 (75 °C) shifted towards a higher value compared to that of ZK-TEPA-60 (60 °C), which may be due to the different natures of TEPA and PEI molecules. The increase in adsorption capacity at the first temperature period indicated the dominant contribution of chemisorption for CO$_2$ adsorption capacity, which was based on two reasons. One reason is that the CO$_2$ molecule overcame the kinetic limitation and the faster diffusion of CO$_2$ molecule was achieved at higher temperatures. Another reason is that the TEPA and PEI molecules were more flexible and their dispersions were more uniform in the mesopores, and more active adsorption sites on amine groups were exposed to CO$_2$ molecules at higher temperatures.

The capacity decreased at the second temperature period. The adsorption progress was dependent on thermodynamics at relatively high temperatures. At this period, CO$_2$ molecules were activated with slightly higher kinetic energy and the part of them overcame the chemical bonds and van der Waals’ force between the surface of ZK-TEPA-60 or ZK-PEI-60 and CO$_2$ molecules. The adsorption capacities of ZK-TEPA-60 at 30, 45, 60, 75 and 90 °C were, 4.44, 4.53, 5.32, 4.85 and 4.62 mmol g$^{-1}$, respectively, while 3.85, 3.95, 4.49, 4.59 and 4.43 mmol g$^{-1}$ for ZK-PEI-60. Their adsorption capacities are all higher than 3 mmol g$^{-1}$, especially for ZK-TEPA-60, indicating that both ZK-TEPA-60 and ZK-PEI-60 are potentially efficient sorbents for CO$_2$ capture.

A comparison of CO$_2$ adsorption capacity via various amine modified adsorbents is given in Table 2. Under similar conditions, both ZK-TEPA-60 and ZK-PEI-60 obtained in this work displayed outstanding adsorption capacities at a low CO$_2$ partial pressure.

What's more, in the practical adsorption operation, the adsorption kinetics should be carefully taken into account. In this work, the adsorption time was selected to achieve 50 and 85% of the equilibrium adsorption capacities for the two best samples in the two series (ZK-TEPA-60 and ZK-PEI-60) at three temperatures as shown in Fig. 8 and Table 3. At 30 and 90 °C,

![Fig. 7 CO$_2$ adsorption curves of (A) ZK-TEPA-60 and (B) ZK-PEI-60 at (a) 30 °C, (b) 45 °C, (c) 60 °C, (d) 75 °C and (e) 90 °C (inlet CO$_2$ concentration: 15 vol%, gas flow rate: 60 cm$^3$ min$^{-1}$).](image)

<table>
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<tr>
<th>Support</th>
<th>Modifier</th>
<th>$W_1$ (%)</th>
<th>Condition</th>
<th>Capacity (mmol g$^{-1}$)</th>
<th>Method</th>
<th>Ref.</th>
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<td>4.49</td>
<td>Impregnation</td>
<td>This work</td>
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</table>

$W_1$: weight percent of modifiers. Condition: pressure was the CO$_2$ partial pressure with dry condition. Y60: Y-type zeolite with a Si/Al molar ratio of 60. AEAPS: N-(2-aminoethyl)-3-aminopropyltrimethoxysilane. 5A@MSA: 5A zeolite was combined with 5A zeolite and mesoporous silica.
both samples displayed small differences in time to achieve 50 and 85% of the maximum adsorption capacities, indicating the similar kinetics. At 30 and 90 °C, respectively, ZK-TEPA-60 required 45.6 and 33 minutes and ZK-PEI-60 required 44.4 and 33.6 minutes to achieve 85% of the maximum adsorption capacities (Table 3, Fig. 8). While at 60 °C, the differences in time to achieve 85% of the maximum adsorption capacities were obvious between both samples (25.9 minutes for ZK-TEPA-60 and 31.2 minutes for ZK-PEI-60) (Table 3, Fig. 8). Therefore, TEPA-loaded samples displayed better kinetics than PEI-loaded samples. Normally, more time is required to adsorb additional CO₂ to reach high adsorption capacity, while ZK-TEPA-60, which possesses higher CO₂ adsorption capacity, interestingly, has better kinetics. This result was due to the well dispersion of TEPA molecules in the inner channels of composites for the easy diffusion of CO₂ molecules, suggesting the importance of uniform dispersion of amine molecules for enhanced kinetics.

The heat of adsorption, usually defined as the enthalpy ($H_{\text{ads}}$) of adsorption, was obtained by calorimetric heat flow measurement for further characterization of adsorption. The differential scanning calorimetry (DSC) heat flow curves of ZK-TEPA-60 and ZK-PEI-60 at three different temperatures are shown in Fig. 9. The enthalpies of adsorption are given in Table 3. The adsorption enthalpies of ZK-TEPA-60 at 30, 60 and 90 °C were, 71.2, 81.2 and 73.3 kJ mol$^{-1}$, respectively, while 67.3, 71.9 and 70.9 kJ mol$^{-1}$ for ZK-PEI-60. These values were all higher than 60 kJ mol$^{-1}$, which were consistent with the chemisorption mechanism, revealing the dominance of

![Fig. 8 Adsorption time of ZK-TEPA-60 and ZK-PEI-60 at (A) 30 °C, (B) 60 °C and (C) 90 °C using 15% CO₂.](image)

![Fig. 9 DSC heat flow curves of (A) ZK-TEPA-60 and (B) ZK-PEI-60 at (a) 30 °C, (b) 60 °C and (c) 90 °C using 15% CO₂.](image)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature (°C)</th>
<th>50%</th>
<th>85%</th>
<th>Enthalpy (kJ mol$^{-1}$)</th>
<th>Average enthalpy (kJ mol$^{-1}$)</th>
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<td>33.6</td>
<td>70.9</td>
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<td>45.6</td>
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<td>8.3</td>
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</table>
played a stable capacity of 4.45 mmol g\(^{-1}\) during CO\(_2\) adsorption process.\(^{59}\) These values correlated well with previously reported data.\(^{51,52}\) The average enthalpy of 75.2 kJ mol\(^{-1}\) was obtained for ZK-TEPA-60 and 70 kJ mol\(^{-1}\) for ZK-PEI-60, both of which were slightly lower than the values obtained by Knowles et al. for aminopropyl-functionalized silica gel.\(^{52}\) These differences can be associated with various natures of amines. For both samples, the trends on enthalpies are similar to those on adsorption capacities and the high enthalpies suggest the high strength of CO\(_2\)-amine interaction (Fig. 7).

Apart from high adsorption capacity, the stability and reproducibility of adsorbents are also essential for the sustainable application process. ZK-TEPA-60 and ZK-PEI-60 were selected for the five cyclic CO\(_2\) adsorption/desorption studies. The graphs of five cycles for ZK-TEPA-60 and ZK-PEI-60 are shown in Fig. 10. After the five cycles, ZK-PEI-60 displayed a stable capacity of 4.45 mmol g\(^{-1}\), which was similar to the initial one (4.49 mmol g\(^{-1}\)). However, a relatively large drop of 7% in adsorption capacity occurred for ZK-TEPA-60, compared to that of ZK-PEI-60 (less than 1%), which may be attributed to the partial volatilization of TEPA in desorption step. ZK-PEI-60 has a better stability and reproducibility than ZK-TEPA-60 during 5 cyclic adsorption/desorption process. But obviously, ZK-TEPA-60 still displayed a large capacity of 4.94 mmol g\(^{-1}\) in the 5th cycle, which is still higher than the reported data as listed in Table 2. The stability of ZK-TEPA-60 is comparable to that of TEPA modified MCM-41 (8.5% drop in adsorption capacity after 6 cycles) reported by Yue et al.\(^{54}\) These results suggest that both ZK-TEPA-60 and ZK-PEI60 are good CO\(_2\) adsorbents and the latter may be the more promising one. Besides, water vapor also exists in flue gas and the CO\(_2\) uptake may be enhanced due to the existence of appropriate content of water vapor.\(^{54,55}\) The effect of water vapor will be reported in the future.

4. Conclusions

The ZSM-5/KIT-6 support was modified with amines (TEPA or PEI) by wet impregnation. The amine efficiency, kinetics of adsorption, enthalpy of adsorption, stability of adsorbent, reusability of adsorbent, the effect of TEPA or PEI loading as well as temperature on CO\(_2\) adsorption performance were investigated. ZK-TEPA-60 displayed the maximum adsorption capacity at 60 °C while a lower value for ZK-PEI-60 was obtained (5.32 mmol g\(^{-1}\) vs. 4.49 mmol g\(^{-1}\)) because of higher nitrogen content and better texture properties. The amine efficiency was up to 0.38 and 0.35 for ZK-TEPA-60 and ZK-PEI-60, respectively.

The optimum temperature was 60 °C for ZK-TEPA-60 while 75 °C for ZK-PEI-60 (with a capacity of 4.59 mmol g\(^{-1}\)), probably associated with different natures of amine molecules. ZK-TEPA-60 has better kinetics than ZK-PEI-60 due to the well dispersion of TEPA molecules. Higher average enthalpy was obtained for ZK-TEPA-60 (75.2 kJ mol\(^{-1}\)) compared to that of ZK-PEI-60 (70 kJ mol\(^{-1}\)), suggesting the high strength of CO\(_2\)-amine interaction. ZK-PEI-60 has a better stability and reproducibility than ZK-TEPA-60 during five cyclic adsorption/desorption process.

Conflicts of interest

There are no conflicts of interest to declare.

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