

Novel CO₂ Adsorbent Prepared with ZSM-5/MCM-48 as Support: High Adsorption Property and Its Mechanism

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Abstract: Adsorption by solid amine adsorbent is a promising technology for decarbonization of flue gas. However, adsorption properties of many solid amine adsorbents need to be enhanced, and it is necessary to further study the CO₂ adsorption mechanism. A novel CO₂ adsorbent with high capacity was obtained by grafting 3-aminopropyltriethoxysilane (APTES) on a micro-mesoporous composite molecular sieve ZSM-5/MCM-48 as the support, and then impregnated with tetraethylenepentamine (TEPA) or polyethyleneimine (PEI). The maximum adsorption capacity of APTES-ZSM-5/MCM-48-TEPA-60 (A-ZM-T60), loaded with 60% (in mass) TEPA, for CO₂ reaches 5.82 mmol·g⁻¹ at 60 °C in 15% (in volume) CO₂. Carbamate, alkyl ammonium carbamate and carbonate are generated during the chemical adsorption, which is dominant for CO₂ adsorption because of the reaction between CO₂ and amino groups on the adsorbent, simultaneously accompanied by weak physical adsorption. All above data confirm that these composites display an outstanding adsorption performance with a bright future for CO₂ capture from flue gas after desulfurization.

Key words: ZSM-5/MCM-48; amino-bifunctionalization; CO₂ capture; adsorption kinetics; adsorption mechanism

Carbon capture and sequestration is often considered as a key technology for decarbonization of the global energy system, with applications ranging from power generation to industrial production. Especially in the industrial sector, carbon capture and sequestration is currently the unique technology that can drastically reduce carbon emissions^[1]. Up to now, three strategies have been proposed for capturing CO₂: post-combustion, pre-combustion, and oxy-fuel CO₂ capture^[2]. Post-combustion capture equipment can be easily integrated into existing infrastructure without substantial changes to the basic combustion technology^[3]. CO₂ adsorption is one of the common post-combustion capture methods, which has the advantages of easy regeneration, low energy consumption, low equipment corrosion, and environmental friendliness^[4]. Common solid adsorbents include activated carbon^[5], metal-organic framework-based adsorbents^[6], MgO-based adsorbents^[7], and molecular sieves^[8].

ZSM-5 with large surface area and total pore volume

is more favorable for the physical adsorption of CO₂^[9]. However, the small pore size of microporous molecular sieves would hinder the transport and diffusion of macromolecules^[10]. This limitation has been addressed by using mesoporous molecular sieves as supports, which have larger pore size and can improve their gas diffusion performance^[11]. MCM-48 is one of the extensively investigated mesoporous molecular sieves, which possesses the structural characteristics of high surface area, large pore volume and adjustable pore size, and has faster mass transfer velocity compared with other mesoporous materials^[12]. Therefore, the adsorption capacity of micro-mesoporous composite molecular sieve for CO₂ is higher compared with the single microporous or mesoporous material. In addition, less liable to pore blocking, MCM-48 provides easy access to guest molecules provided from amines^[13]. Amino-modified adsorbents are commonly used to further improve the adsorption performance of CO₂. The methods for preparing amine-modified adsorbents include impregnation^[14], gra-

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fting^[15], direct synthesis^[16], and amino-bifunctionalization^[17]. Among them, amino-bifunctionalization combines physical impregnation and chemical grafting, overcoming the disadvantages of lower adsorption capacity and amine utilization efficiency in a single method. The adsorbent prepared through amino-bifunctionalization exhibits high amino efficiency^[18], which has attracted more attention. However, the adsorption properties of a lot of solid amine adsorbents are not satisfactory, and there is little research on their adsorption mechanism.

In this work, the novel ZSM-5/MCM-48 (ZM) composite was firstly grafted with APTES and then impregnated with PEI or TEPA for amino-bifunctionalization, and the CO₂ adsorption performance of amino-bifunctionalized composites was evaluated. *In situ* Fourier transform infrared (FT-IR) spectroscopy was used to characterize the adsorption products for exploring the adsorption mechanism.

1 Experimental

1.1 Synthesis of ZSM-5/MCM-48 (ZM)

To prepare the ZSM-5/MCM-48 micro-mesoporous composite molecular sieve^[19], 5.5 mL of tetraethyl ammonium chloride, 10 mL of ethyl silicate and 0.1145 g of aluminum isopropoxide were mixed in an autoclave and kept at 100 °C for 4 h. It was added into the aqueous solution consisting of sodium hydroxide (0.9346 g) and cetyltrimethyl ammonium bromide (1.9818 g), and heated at 150 °C for 8 h. After cooling to room temperature, the mixture was filtered, and the deposit was dried at 100 °C for 24 h. Finally, the material was calcined at 550 °C for 6 h in the muffle furnace to afford ZM.

1.2 Bifunctional modification (synthesis of A-ZM-Tx/A-ZM-Px)

1 g of ZM, 1 mL of APTES and 50 mL of ethanol were refluxed at 85 °C for 12 h. The deposit was filtered, washed with ethanol, and dried at 100 °C for 12 h to afford the grafted sample, named as APTES-ZM-1 (A-ZM-1).

TEPA or PEI was anchored onto A-ZM-1 support *via* impregnation. A certain amount of TEPA or PEI was dispersed in 50 mL of ethanol and stirred until the modifier was completely dissolved. After adding 0.5 g of A-ZM-1 and stirring thoroughly, the sample was dried at 80 °C for 16 h. The product was referred to as APTES-ZSM-5/MCM-48-TEPA-*x*/PEI-*x* (A-ZM-T_{*x*}/A-ZM-P_{*x*}, *x*=50, 55, 60, 70), where *x* represents the mass fraction of TEPA or PEI. For instance, A-ZM-T60 indicated that the grafted sample A-ZM-1 was further loaded with 60% (in

mass) TEPA.

2 Results and discussion

2.1 Analysis of crystal structure

Small-angle XRD patterns of the synthetic materials (Fig. 1(a)) indicate that the composite material ZM shows sharp diffraction peaks at $2\theta=2.6^\circ$ and 3.0° , which correspond to the crystal faces (221) and (220) of MCM-48^[20]. Compared with MCM-48, the diffraction peak intensity of ZM decreases possibly due to the addition of ZSM-5 which impacts the order of mesoporous structure in molecular sieve, while the cubic structure shows no obvious change. Wide-angle XRD patterns of the synthetic materials (Fig. 1(b)) show that the three samples have strong diffraction peaks at $2\theta=7.9^\circ$, 8.8° , 23.0° , 23.6° , and 24.3° , which correspond to the crystal faces (101), (200), (051), (303), and (133) of ZSM-5, respectively^[21]. The intensity of characteristic peaks of ZM is lower than that of ZSM-5 due to the existence of MCM-48 phase. A-ZM-1 displays similar characteristic peaks to ZM, though the intensity decreases slightly. Therefore, the XRD patterns indicate that ZM is synthesized successfully, and the grafting process does not change the crystal structure of ZM.

2.2 Analysis of surface morphology

As can be seen from Fig. 2(a), the cubic phase MCM-48 molecular sieve is formed by the aggregation

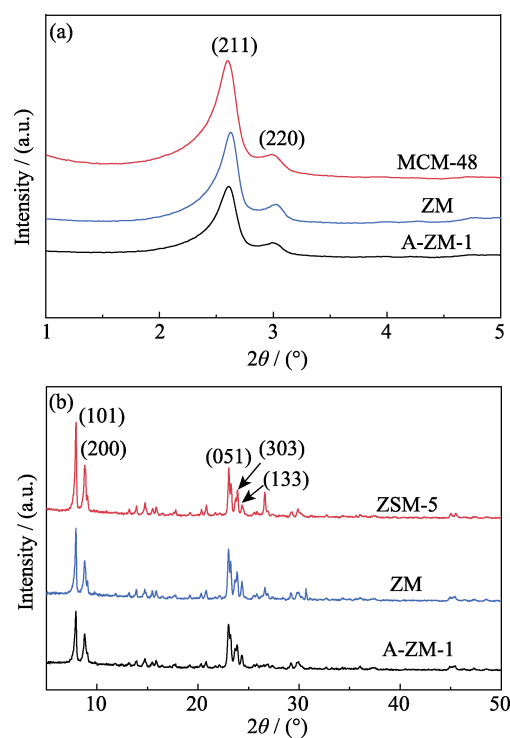


Fig. 1 XRD patterns of ZSM-5, MCM-48, ZM, and A-ZM-1 (a) Small-angle; (b) Wide-angle

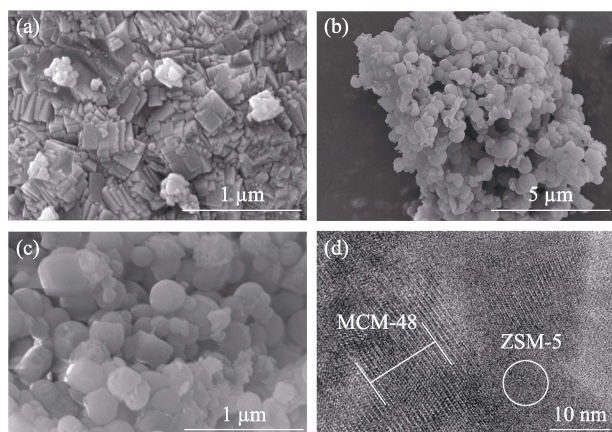


Fig. 2 Characterization of surface morphology (a-c) SEM images of (a) MCM-48, (b) ZSM-5, and (c) ZM; (d) TEM image of ZM

of submicron spherical particles^[20]. ZSM-5 shows uniform particles formed by the stacking of cubic pieces (Fig. 2(b))^[22], and ZM has both cubic particles and spherical particles (Fig. 2(c)), indicating that ZSM-5 and MCM-48 have been successfully combined^[23]. In TEM image (Fig. 2(d)), ZM includes both MCM-48 and ZSM-5 channels that are well ordered. The results obtained are consistent with XRD analysis.

2.3 Low temperature nitrogen adsorption-desorption

N₂ adsorption-desorption isotherms of the amino-bifunctionalized ZM are shown in Fig. 3. As the amino-loading in A-ZM-Tx increases, the pore channels of the amino-bifunctionalized support are partially blocked by the modifier, which exhibits smaller hysteresis loops (Fig. 3(a)). However, for both A-ZM-P50 and A-ZM-P60, there are nearly no hysteresis loops observed (Fig. 3(b)), which is attributed to PEI modifier with larger molecular weight blocks some pores. The corresponding specific surface areas, total pore volumes and CO₂ adsorption capacities are listed in Table 1. When TEPA loading increases from 50% to 70%, the specific surface area of amino-bifunctionalized material decreases from 111.2 to 5.8 m²·g⁻¹, and the total pore volume decreases from 0.21 to 0.02 cm³·g⁻¹. For A-ZM-P70, the specific surface area and pore volume are too small to be detected.

2.4 CO₂ adsorption capacities and cyclic performance

The CO₂ adsorption capacities are calculated according to Eq. (S1) in supporting materials. The CO₂ adsorption curves of A-ZM-Tx and A-ZM-Px at 60 °C are shown in Fig. 4(a). The highest CO₂ saturated adsorption capacity of amino-bifunctionalized ZM adsorbent is 5.82 mmol·g⁻¹ for A-ZM-T60, which is 487% higher than that of ZM. The large number of amine groups loaded on ZM provides more active sites for CO₂ adsorption. In

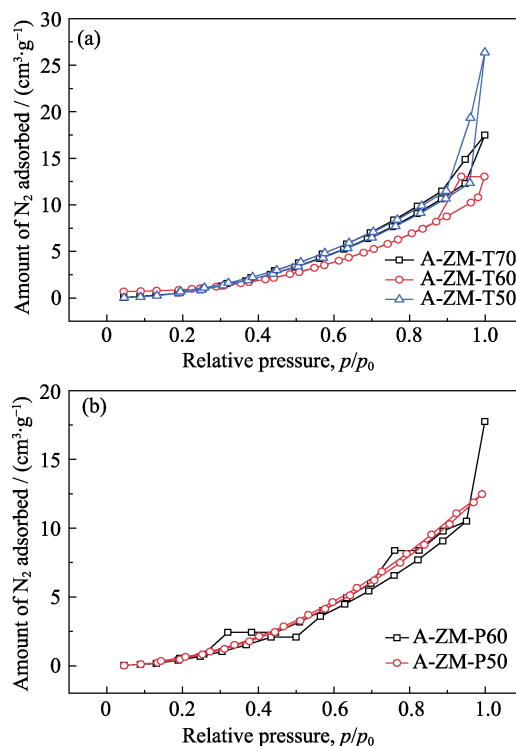


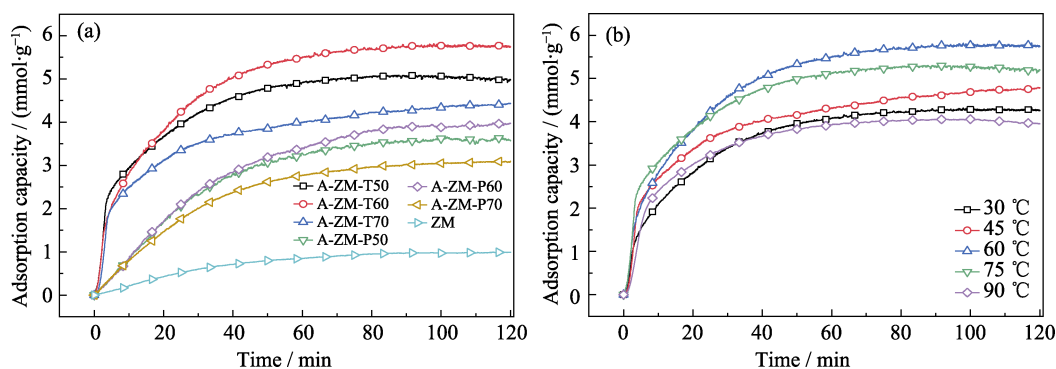
Fig. 3 N₂ adsorption-desorption isotherms of (a) A-ZM-Tx and (b) A-ZM-Px

Table 1 Physical properties, nitrogen contents and CO₂ adsorption capacities of amino-bifunctionalization ZM adsorbents at 60 °C

Adsorbent	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_t/(\text{cm}^3 \cdot \text{g}^{-1})$	N ₂ content/(mmol·g ⁻¹)	CO ₂ adsorption capacity/(mmol·g ⁻¹)
A-ZM-1	237.0	0.52	4.97	1.71
A-ZM-T50	111.2	0.21	8.94	5.04
A-ZM-T60	13.0	0.04	11.89	5.82
A-ZM-T70	5.8	0.02	14.85	4.51
A-ZM-P50	91.5	0.20	8.52	3.53
A-ZM-P60	12.3	0.03	11.17	3.96
A-ZM-P70	—	—	14.06	3.05

* S_{BET} : specific surface area; V_t : total pore volume

addition, the Si—O—Si generated after the reaction of APTES with silanol on ZM forms a network structure, which promotes the uniform distribution of the grafting modifier on the surface and in the channels of ZM, and reduces the diffusion resistance of CO₂ in the channels. Impregnated amines such as PEI and TEPA have the characteristic of easy migration, which can disperse the grafted amines and promote the reaction of grafted amines with CO₂, resulting in the synergistic interaction on the ZM support. Therefore, the CO₂ adsorption capacity of the amino-bifunctionalized adsorbent is enhanced compared to those of the adsorbents modified by grafting or impregnation alone. Owing to the high molecular

Fig. 4 CO₂ adsorption curves

(a) A-ZM-Tx, A-ZM-Px and ZM at 60 °C; (b) A-ZM-T60 at 30, 45, 60, 75 and 90 °C

weight and viscous characteristics of PEI, the pores of A-ZM-Px are easily blocked, limiting the diffusion of CO₂ and reducing the contact between CO₂ and active sites, thus the adsorption capacity decreases. This explains why the CO₂ saturated adsorption capacity of A-ZM-Px is lower than that of A-ZM-Tx.

Adsorption temperature is an important factor that affects the adsorption capacity of CO₂. The CO₂ adsorption curves of A-ZM-T60 at 30, 45, 60, 75, and 90 °C are shown in Fig. 4(b). In the temperature range of 30–90 °C, the CO₂ saturated adsorption capacity firstly increases and then decreases, and the maximum adsorption capacity is 5.82 mmol·g⁻¹ at 60 °C. Due to the higher viscosity of TEPA and easier aggregation on the support surface at lower temperatures, the adsorption capacity of A-ZM-T60 is low. As the adsorption temperature increases, the activity of amine modified groups is also enhanced, leading to more uniform distribution on the surface and inside pores of the support with more amine-active sites exposed. Simultaneously, with the increase of temperature, the diffusion resistance of CO₂ decreases, reducing the steric hindrance effect and increasing the kinetic energy of CO₂, which leads to an increase in accessibility to the active site of the amino groups^[24]. The adsorption capacity gradually decreases in the temperature range of 60–90 °C, which is mainly due

to the heat generated from the interaction between the modified amine on adsorbents with CO₂, and adsorption is less effective at higher temperatures. Additionally, a part of CO₂ is physically attached to A-ZM-T60 surface and excessively high temperatures cause van der Waals forces to decrease gradually, resulting in a decrease in the adsorption capacity.

Table 2 summarizes the corresponding CO₂ adsorption capacities of amino-bifunctionalized adsorbents in literature. A-ZM-T60 obtained in this work shows excellent adsorption capability at lower partial pressure of CO₂ compared with the other adsorbents.

Cyclic experiments on A-ZM-T60 and A-ZM-P60 are conducted using thermal gravimetric analyzer (Fig. S1). After 10 cycles of desorption, the saturated adsorption capacity of A-ZM-T60 decreases from 5.82 to 5.32 mmol·g⁻¹. Nevertheless, the adsorption capacity of A-ZM-P60 decreases from 3.96 to 3.83 mmol·g⁻¹. It is found that A-ZM-P60 is more stable because PEI possesses larger molecular weight, better thermal stability, and less decomposition volatilization during desorption.

2.5 CO₂ adsorption kinetics

The adsorption data of A-ZM-T60 at different temperatures are fitted using pseudo-first-order, pseudo-second-order and Avrami models (Eq. (S2)–Eq. (S4)). Fig. 5 shows the fitting results of the three models of adsorbent

Table 2 CO₂ adsorption capacities of various amino-bifunctionalized adsorbents

Support	Modifier	Condition (CO ₂ , in volume)	CO ₂ adsorption capacity/(mmol·g ⁻¹)	Ref.
MCF	APTMS+PEI	75 °C/10.5% CO ₂	2.36	[25]
SBA-15	APTES+TEPA	75 °C/20% CO ₂	5.68	[26]
HNTS	APTES+PEI	50 °C/50% CO ₂	1.03	[27]
PE-SBA-15	APTES+TEPA	40 °C/15% CO ₂	5.50	[28]
PE-SBA-15	DT+TEPA	40 °C/15% CO ₂	4.20	[28]
Beta/KIT-6	APTMS+TEPA	60 °C/15% CO ₂	5.12	[29]
ZSM-5/MCM-48	APTES+TEPA	60 °C/15% CO ₂	5.82	This work

*APTMS: 3-aminopropyltrimethoxysilane; APTES: 3-aminopropyltriethoxysilane; DT: trimethoxysilylpropyl-diethylenetriamine; PEI: polyethyleneimine; TEPA: tetraethylenepentamine

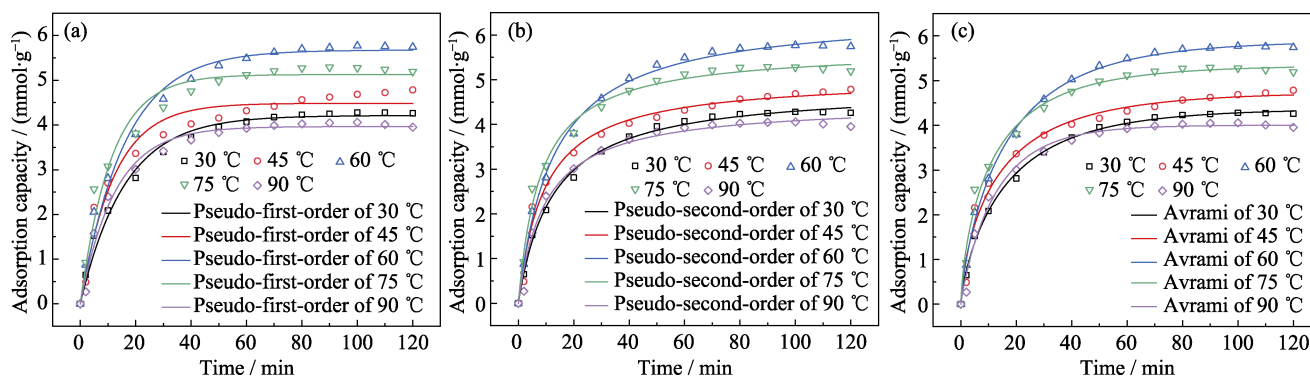


Fig. 5 (a) Pseudo-first-order, (b) pseudo-second-order and (c) Avrami fitting curves of A-ZM-T60 at various temperatures

A-ZM-T60 at various temperatures, with the corresponding fitting data presented in Table 3. The fitting data for the pseudo-first-order model of A-ZM-T60 at 30, 45, 60, 75, and 90 °C are lower than the experimental values, with low correlation coefficients (R^2). The fitting degree of A-ZM-T60 with pseudo-first-order kinetics model is lower (Fig. 5(a)), indicating that the adsorption process of A-ZM-T60 on CO₂ is not pure physical adsorption. The saturated adsorption capacities of CO₂ fitted by the pseudo-second-order kinetic model are different from those measured experimentally with low R^2 . Therefore, the pseudo-second-order kinetic model could not describe well the CO₂ adsorption process of A-ZM-T60 (Fig. 5(b)), indicating that the process is not simple chemisorption.

The fitting data of the Avrami model for A-ZM-T60 at 30, 45, 60, 75, and 90 °C are close to the experimental data, with R^2 higher than 0.99. Therefore, the Avrami model can better describe the CO₂ adsorption process of A-ZM-T60 (Fig. 5(c)), which involves both chemisorption and physical adsorption and is dominated by chemisorption. Table 3 shows that n_A does not fluctuate significantly, indicating that the adsorption mechanism at different temperatures is consistent.

2.6 Adsorption mechanism analysis

To study the interaction between CO₂ and functional modification composite samples, *in situ* FT-IR was used to analyze A-ZM-T60 before and after CO₂ adsorption at 60 °C.

After adsorption, four new vibration peaks of A-ZM-T60 at 2305, 1601, 1478, and 1351 cm⁻¹ appear (Fig. 6). There is a typical physical adsorption peak for CO₂ at 2305 cm⁻¹ caused by the asymmetric tensile vibration, which is due to the interaction between CO₂ molecules with hydroxyl groups (–OHOCO)^[30]. Carbamate is synthesized by the reaction of amine on the material and CO₂^[31], and its characteristic adsorption peak is found at 1601 cm⁻¹. Unpaired electrons in the N atom of amino group collide with electrophilic C atom of CO₂ to generate the carbamate (RNHCOOR') (Eq. (1)). The flowable TEPA and PEI may distribute throughout the grafted amine during impregnation, improving the interaction in Eq. (1). Furthermore, the combined action of the mobile amines in TEPA/PEI and the fixed amines in APTES enhances CO₂ adsorption.



The –NCOO– skeleton vibration of alkyl ammonium carbamate (RNHCOOH₃NR, R represents alkyl) produces the infrared adsorption peak between 1540 and

Table 3 Kinetic parameters of CO₂ adsorption on A-ZM-T60 at various temperatures

Model	Kinetics parameter	30 °C	45 °C	60 °C	75 °C	90 °C
Pseudo-first-order	$q_e/(\text{mmol} \cdot \text{g}^{-1})$	4.21	4.49	5.68	5.13	3.95
	k_1/min^{-1}	0.062	0.083	0.062	0.089	0.080
	R^2	0.989	0.966	0.989	0.973	0.987
Pseudo-second-order	$q_e/(\text{mmol} \cdot \text{g}^{-1})$	4.83	5.06	5.70	6.51	4.48
	$k_2/(\text{g} \cdot \text{mmol}^{-1} \cdot \text{min}^{-1})$	0.017	0.021	0.022	0.012	0.023
	R^2	0.997	0.988	0.991	0.997	0.987
Avrami	$q_e/(\text{mmol} \cdot \text{g}^{-1})$	4.37	4.75	5.89	5.34	4.00
	k_A/min^{-1}	0.109	0.153	0.109	0.167	0.099
	n_A	0.776	0.696	0.776	0.704	0.901
	R^2	0.998	0.991	0.998	0.990	0.998

* q_e : CO₂ saturated adsorption capacity; k_1 , k_2 and k_A : rate constants of three models, respectively; n_A : Avrami model series; R^2 : correlation coefficient

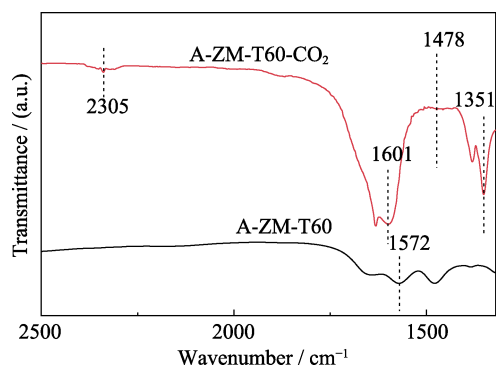
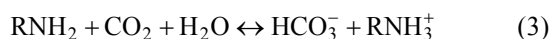


Fig. 6 FT-IR spectra of A-ZM-T60 before and after CO₂ adsorption

1440 cm⁻¹^[32]. The bands are explained by the formation of asymmetric and symmetric deformations that arise from the interaction of two alkyl ammonium carbamate amines with CO₂ molecules^[33] (Eq. (2)). The adsorption peak at 1351 cm⁻¹ arises from the bending vibration of carbonate C–O, which is caused by the reaction between CO₂ and residual water presented in the material^[34]. Due to its distinctive reaction mechanism, the residual moisture in the material improves its adsorption performance. The reaction equation is shown in Eq. (3).



In summary, the CO₂ adsorption of A-ZM-T60 has both physical and chemical adsorption. Physical adsorption is the adsorption of CO₂ molecules onto composite molecular sieves with van der Waals force, whereas chemisorption is the chemical reaction of amine groups with CO₂ to generate carbonate, carbamate and alkyl ammonium carbamate. Thus, A-ZM-T60 possesses multiple CO₂ adsorption sites, such as the physical adsorption site (μ–OH) and the chemisorption sites (N–H and N–C). As the strength of the absorption peak shown in Fig. 6, the primary adsorption process is chemisorption, and physical adsorption plays a minor role.

3 Conclusions

A two-step hydrothermal crystallization process was used to prepare ZSM-5/MCM-48 composite, which is subsequently bifunctionally modified with grafting of APTES and impregnating of TEPA/PEI. With an increase in TEPA or PEI loading, the CO₂ adsorption capacities firstly increase and then decline, which reaches a maximum at a loading of 60% of TEPA or PEI. Among them, the maximum CO₂ adsorption capacity of A-ZM-T60 is 5.82 mmol·g⁻¹, surpassing most of the reported adsorbents under similar conditions, and showing A-ZM-T60 is a prospective high-efficiency CO₂ adsorbent with good CO₂ adsorption capability. The

analysis of *in situ* FT-IR shows that the main reason for the increase in adsorption capacity is the chemical reaction between CO₂ and surface amino groups, which forms carbamate, alkyl ammonium carbamate and carbonate. Therefore, the adsorption process involves both chemical and physical adsorption, with chemical adsorption being the dominant factor. The result offers theoretical guidance for the industrial application of solid amine adsorbents.

Supporting materials

Supporting materials related to this article can be found at <https://doi.org/10.15541/jim20240403>.

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以 ZSM-5/MCM-48 为载体制备新型高容量 CO₂ 吸附剂的性能及机理研究

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摘 要: 固体胺吸附法是一种极具发展前景的烟气脱碳技术, 但该技术中吸附剂的 CO₂ 吸附性能不高, 且吸附机理研究亦不深入。以微介孔复合分子筛 ZSM-5/MCM-48 为载体, 通过先接枝 3-氨基丙基三乙氧基硅烷(APTES), 再将接枝后的样品浸渍四乙烯五胺(TEPA)或聚乙烯亚胺(PEI), 从而得到一种 CO₂ 吸附性能优异的新型材料。当 TEPA 的负载量为 60%(质量分数)时, APTES-ZSM-5/MCM-48-TEPA-60(A-ZM-T60)在 60 ℃和 15%(体积分数)CO₂ 环境下对 CO₂ 的最大吸附量为 5.82 mmol·g⁻¹。吸附过程以化学吸附为主, 吸附剂表面胺基与 CO₂ 反应生成了氨基甲酸酯、氨基甲酸烷基铵和碳酸盐, 同时伴有较弱的物理吸附。该复合材料吸附性能优异, 可用于捕集脱硫后烟气中的 CO₂。

关 键 词: ZSM-5/MCM-48; 胺双功能化; CO₂ 吸附; 吸附动力学; 吸附机理

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Supporting materials:**Novel CO₂ Adsorbent Prepared with ZSM-5/MCM-48 as Support:
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Materials and methods

Materials Tetraethylammonium chloride (TEOAH, Aladdin Industrial Co., Ltd., Shanghai, China), ethyl silicate (TEOS, Aladdin Industrial Co., Ltd., Shanghai, China), aluminium isopropoxide (AIP, Xilong Chemical Co., Ltd., China), sodium hydroxide (NaOH, Aladdin Industrial Co., Ltd., Shanghai, China), hexadecyl trimethyl ammonium bromide (CTAB, Aladdin Industrial Co., Ltd., Shanghai, China), APTES (Aladdin Industrial Co., Ltd., Shanghai, China), TEPA (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and PEI (Aladdin Industrial Co., Ltd., Shanghai, China) were used in this work. Standard CO₂/N₂ gas mixture (15% (in volume), purity of 99.999%, Guangxi Ruida Chemical Technology Co., Ltd, China) was used as the feed gas.

Instrumentation X-ray diffraction (XRD) pattern is recorded on an X'Pert3 powder diffractometer (PANalytical, Holland) using a Cu-K α radiation (40 kV, 40 mA). The diffraction data are collected in the 2 θ range of 0.6°–5° and 5°–50° with a scanning rate of 10 (°)/min. The morphology of each sample is obtained by a JEM-2100F scanning electron microscope (SEM, Hi-tech Corporation, Japan) under accelerating voltages of 10 kV and 120 kV. Fourier transform infrared spectroscopy (FT-IR) spectra of all samples are recorded on the Nexus 470 IR spectrometer (Nicolet, USA) over the wavenumber range of 400–4000 cm⁻¹ at room temperature, after mixing the samples and KBr at a mass ratio of 1 : 100. The BET specific surface area and the pore properties are measured by N₂ adsorption-desorption experiments at -196 °C with a JW-BK200C volumetric adsorption analyzer (JWGB Sci & Tech, China). Each sample is outgassed at 100 °C in a vacuum atmosphere for 2 h before the test. The surface area is calculated by the Brunauer–Emmett–Teller (BET) method. Total pore volume is calculated from N₂ adsorption capacity at $p/p_0=0.99$. Pore size distribution is derived from the adsorption branch of N₂ curve using the Barrett–

Joyner–Halenda (BJH) method.

Synthesis of ZSM-5 and MCM-48 Hydrothermal synthesis was used to prepare the ZSM-5 zeolite molecular sieve and the MCM-48 mesoporous molecular sieve, respectively. The precise actions taken were as follows. For the ZSM-5 zeolite molecular sieve, solution S₁ was prepared by stirring after 1.0 g of sodium meta-aluminate was dissolved in 20 mL of 1 mol/L sodium hydroxide solution. In addition, 0.6 g sodium hydroxide and 5.3 g tetrapropyl-ammoniumhydroxide were dissolved in 16 g deionized water. After mixing, 20 g silicon dioxide was added, and the S₂ solution was formed by stirring. After stirring thoroughly at room temperature, the solutions S₁ and S₂ were moved into a high-pressure reactor and kept at 170 °C for 32 h. Then it was cooled to room temperature, the resulting product was filtered, washed in distilled water and baked at 80 °C to dry. Finally, it was placed into a Muffle furnace, and roasted at 550 °C for 6 h before removing the templating agent to make ZSM-5 micromolecular sieve^[S1]. To prepare MCM-48 mesoporous molecular sieve, 10 mL ethyl silicate was stirred in 50 mL water at room temperature, and then 0.9 g sodium hydroxide was added. After all sodium hydroxide was dissolved, 10.61 g of cetyltrimethyl ammonium bromide was added, stirred and then put into a high-pressure reactor for crystallization at 120 °C for 36 h. After the reactor cooling to room temperature, the product was filtrated and then cleaned. The obtained products were dried in a blast oven at 80 °C for 12 h and then kept in a Muffle oven at 550 °C for 6 h, obtaining MCM-48 mesoporous molecular sieve^[S2].

CO₂ adsorption experimental setup CO₂ adsorption capacity of ZM and A-ZM-Tx/Px were determined by thermal gravimetric analyzer. The sample (6–8 mg) was desorbed at 110 °C for 1 h in N₂ atmosphere, cooled to the required adsorption temperature, and then switched into a mixture of N₂ and CO₂. The change in sample mass was recorded, and the CO₂ adsorption capacities of the samples were calculated. The equation was as follows:

$$q_e = \frac{(m_e - m_d) / 44.01}{m_d / 1000} \quad (S1)$$

where q_e is the saturated adsorption capacity of CO₂ (mmol·g⁻¹); m_e and m_d are the weights of adsorption saturated and dehydrated adsorbent (mg), respectively; 44.01 is the molar mass of CO₂ (g·mol⁻¹).

Cyclic experimental setup Cyclic performance of the samples was tested as follows. The adsorption temperature of the cycle experiment was set to 60 °C, a gas mixture containing 15% (in volume) CO₂ (99.999%) and the balance of N₂ (99.999%) was used in the adsorption process, and the adsorption time was 120 min. The desorption temperature was set to 110 °C, pure nitrogen was subjected to desorption, and the desorption time was 40 min. The cycle was repeated 10 times to explore cyclic performance.

Calculation method of adsorption kinetics Pseudo-first-order, pseudo-second-order and Avrami models were used to fit the adsorption data and explore the adsorption mechanism. The kinetics equations involved were as follows:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (S2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (S3)$$

$$q_t = q_e(1 - e^{-(k_A t)^{n_A}}) \quad (S4)$$

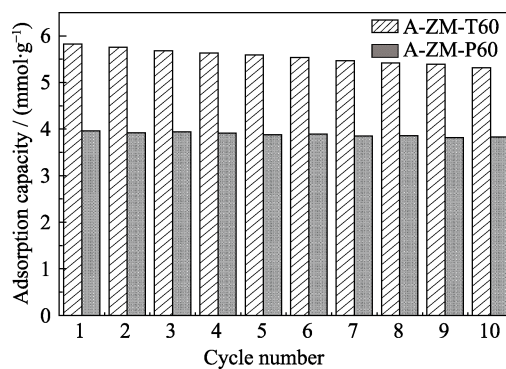


Fig. S1 CO₂ saturated adsorption capacity of A-ZM-T60 and A-ZM-P60 during 10 adsorption-desorption cycles

where q_t and q_e are the CO₂ adsorption capacity at time t and the CO₂ saturated adsorption capacity of the adsorbent (mmol·g⁻¹), respectively; k_1 , k_2 and k_A are the rate constants of three models (min⁻¹, g·(mmol·min)⁻¹ and min⁻¹), respectively; n_A is the Avrami model series.

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