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# Ultra-highly efficient adsorbent for CO<sub>2</sub> capture from air by directional deprotonation regulation of MOFs-based amine grafting



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### ABSTRACT

In recent years, the solid amine of Metal-Organic Frameworks (MOFs) has shown promise as a direct air capture (DAC) adsorbent. However, the efficiency of amine groups under ultra-low CO2 concentrations requires improvement. In this study, we propose a novel method to regulate proton migration through solvent effects during amine grafting, to enhance the synthesis of MOFs as solid amine adsorbents and improve amine group utilization. This approach yielded outstanding results with a MIL-100(Cr)-based DAC adsorbent, demonstrating a  $CO_2$  adsorption capacity of 2.15 mmol/g and an ultra-high amine group utilization of 89.6 % at ambient conditions. By directional deprotonation regulation, the CO<sub>2</sub> adsorption performance of the UiO-66(Zr)-based adsorbent significantly increased from 0.06 mmol/g of using H<sub>2</sub>O as solvent to 1.71 mmol/g of using NMP, with a 27.5-fold increase. Specifically, organic polar aprotic solvents enhanced the binding energy and reduced the energy barrier for deprotonation during the grafting process, thereby improving CO<sub>2</sub> adsorption performance and amine group utilization, which shed a new light on the development of MOFs based CO2 adsorbent. Furthermore, due to the coordination of secondary amine groups with metal sites leads to the decrease of hydrophilic functional groups in the CO2 adsorption products, the hydrophobicity of products was reduced significantly resulting in an increase in the  $\Delta S$  of the hydrated ion pairs after the adsorption, which reduced the heat of CO2 adsorption about 15 % than that reported in the literature. Based on changes in humidity conditions, the regeneration energy consumption of the MF-Cr-AEEA is less than 2.5 GJ/t CO2 under a relatively lower humidity, demonstrating outstanding industrial applications potential of the adsorbent.

#### 1. Introduction

Direct air capture (DAC) technology has gained significant attention as an efficient method for negative carbon emissions by separating  $CO_2$ from the atmosphere using sorption technology [1,2]. DAC offers advantages such as requiring less land, efficiently processing emissions from dispersed combustion sources and allowing flexible deployment of  $CO_2$  utilization and storage [3,4]. In recent years, Metal-Organic Frameworks (MOFs) have attracted considerable interest as potential adsorbents for DAC due to their high specific surface area and strong  $CO_2$  affinity [5–8]. It has been established that MOFs possess unsaturated metal sites resulting from missing linkers, which exhibit metallic acidity and facilitate the grafting of amine groups [9–14].

However, the complex surface functional groups of MOFs and the interaction mechanism between MOFs and amine groups remain largely unknown, warranting further investigation. The incorporation of amine groups into MOFs, especially at unsaturated metal sites originating from missing linkers, is generally achieved through a zwitterion mechanism [11,12,14]. In recent years, various amine groups, such as primary, secondary, tertiary, or quaternary amines, have been loaded onto MOFs.

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Moreover, to increase the CO<sub>2</sub> adsorption capacity, excessive amine loading is often employed, resulting in reduced amine group utilization due to losses during the cleaning process [15-19]. Rim et al. [7] loaded poly(ethylenimine) (PEI) onto MIL-101(Cr) to obtain a solid amine adsorbent based on MOFs, achieving an amine group utilization of 20-30 %. McDonald et al. [15] loaded N,N'-dimethylethylenediamine (mmen) with Mg<sub>2</sub>(dobpdc) to obtain a supported amine adsorbent, but the utilization of the amine group was only 3–10 %. In addition, the excessive amine loading can easily lead to the blockage of the internal pores of the adsorbent, resulting in the participation of only the surface amine functional group in the adsorption reaction, and the internal amine group can not show activity, which reduces the utilization of amine functional groups. Meanwhile, the volatilization loss and oxidative degradation of impregnated amines in the channels also limit the adsorbent's reusability. The adsorbent synthesized by chemical grafting can effectively improve the internal porosity and increase the utilization of amine functional groups. Therefore, to improve the utilization of amine functional groups under ultra-low CO<sub>2</sub> concentrations, the optimization of chemical grafting reaction is crucial.

In a previous study [19], we observed that the metal site types of MOFs and the pH of the dispersed solvent significantly influenced amine group utilization. Lower pH levels hindered the collaborative adsorption of metal sites and amine groups due to neutralization reactions. Thus, controlling the expression of MOFs' metallic acidity to regulate acidity during grafting is crucial for efficient amine group utilization. According to the literature [20-23], different solvents can effectively control system acidity by influencing proton movement. In addition, the amine grafting reaction on MOFs involves multiple reactants and mechanistic steps, making it highly susceptible to solvent properties such as polarity, proticity, aproticity, and carbon content. Da Silva and Svendsen [24] reported that solvent molecules could act as a proton acceptor instead of amines in the reaction between primary alkanolamines and acidic gases. Therefore, a comprehensive investigation of solvent effects on amine grafting with different MOFs metal site types is imperative to identify suitable solvent systems that improve amine group utilization and

activate amine sites effectively.

In addition, the extensive energy input in desorption processes would also be a crucial barrier to realize practical  $CO_2$  capture. Based on the current analysis of adsorbent regeneration energy consumption structure, the excellent  $CO_2$  adsorption performance and high amine group utilization are key to reducing the energy consumption of the adsorbent. However, due to the wide variety of adsorbents, the specific principle of the influence of adsorption performance on energy consumption needs to be further revealed. So, the regeneration energy consumption of the adsorbent and its influencing factors need to be further optimized to guide the future industrialization direction.

Herein, we report that a series of modified MOFs adsorbents with different solvent systems using N-(2-aminoethyl)ethanolamine (AEEA) as a modifier to investigate the effects of solvents on amine group utilization and identify suitable solvent systems (Fig. 1). The study focused on three types of reaction processes: those utilizing an inorganic polar protic solvent system (H<sub>2</sub>O), an organic polar protic solvent system (CH<sub>3</sub>OH), and an organic polar aprotic solvent (NMP) system (Table S1). Moreover, depending on the choice of metal ions, MOFs can obtain various surface characteristics and rich L acid sites, which can be described in terms of the magnitude of pH. Thus, to reveal the effect of MOFs metal sites in amine grafting reaction, MIL-100(Fe), UiO-66(Zr), and MIL-100(Cr) with different metal acid sites and pH were used as carriers. And the adsorptive property of the prepared adsorbents is investigated at a CO<sub>2</sub> concentration of 400 ppm to reveal the amine grafting reaction regularity. To revealed the amine grafting reaction principles for atomic-level, we investigated the stable structures of the adsorbent in grafting process under different solvent conditions, using the density functional theory (DFT). Finally, the adsorbent was characterized by Differential Scanning Calorimeter (DSC) to optimize the regeneration energy consumption structure of adsorbents.



Fig. 1. The synthesis route of different adsorbents using MIL-100(Cr) as a carrier (gray: carbon atoms for MIL-100(Cr), red: oxygen atoms, green: chromium atoms, white: hydrogen atoms). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

#### 2. Experimental section

#### 2.1. Raw materials

Zirconium tetrachloride (ZrCl<sub>4</sub>), Chromium(VI) oxide (CrO<sub>3</sub>), Iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), N,N-dimethylformamide (DMF), Methanol, Ethanol and Hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). N-Methylpyrrolidone (NMP) and N-(2-Aminoethyl)ethanolamine (AEEA) was obtained from Macklin Biochemical Co., Ltd, (Shanghai, China). Trimesic acid (H<sub>3</sub>BTC), Terephthalic acid (H<sub>2</sub>BDC) and Deionized water were obtained from Aladdin BioChem Technology Co., Ltd.

### 2.2. Amine grafting

MIL-100(Cr), MIL-100(Fe) and UiO-66(Zr) were prepared after modifications based on the available literature [19,25,26]. Meanwhile, MOFs solid amine adsorbents were prepared directly based on the reported literature. In detail, 0.5 g AEEA was added to 10 mL solvent and stirred for 10 min. Then, 0.5 g MOFs (MIL-100(Cr), MIL-100(Fe), or UiO-66(Zr)) were added, and the mixture was ultrasound treated in a closed environment for 20 min. Next, the mixture was stirred magnetically at room temperature for 12 h. Finally, the mixture was centrifuged and purged with nitrogen at 70 °C for 1 h to dry solvent (MF-Cr/Fe/Zr-AEEA-solvent).

#### 2.3. Adsorbent characterization

The amount of water adsorbed by the adsorbent under different humidity were determined with Microtracbel Belsorp Max (MicrotracBEL, Co., Ltd., Japan) and DVS Intrinsic (Micromeritics, Co., Ltd., America), and the sample was degassed for 8 h at 100 °C in a vacuum oven before the test. The adsorption heat of the adsorbent was recorded on the Q2000 Differential Scanning Calorimeter (DSC) (TA Instruments, Co., Ltd., America) in which the adsorption temperature was 25 °C. The specific heat capacity of sample was conducted on DSC2500 Differential Scanning Calorimeter (TA Instruments, Co., Ltd., America), which was conducted from 25 °C to 80 °C at linear heating rate of 3 °C/min. Functional groups of adsorbents were measured by Nicolet iS50 FTIR spectroscopy (Thermo Fisher, Co., Ltd., America) with a spectral resolution of 4  $\text{cm}^{-1}$  from 4000 to 400  $\text{cm}^{-1}$ . The XPS carbon spectrum was recorded by Scientific K-Alpha and the NMR experiments were carried out in Bruker Avance Neo 400WB. The surface morphology of the adsorbent was characterized using Sigma 300 scanning electron microscopy (Carl Zeiss, Co., Ltd., Germany) operated at 2 kV. The element content of the adsorbent was analyzed on Elemental Analyzer of UNICUBE (Elementar, Co., Ltd., Germany). The pH of system was evaluated by pH meter.

#### 2.4. CO2 adsorption/desorption experiment

The CO<sub>2</sub> adsorption experiment was carried out in an isothermal adsorption reactor, as shown in Fig. S1. The testing process includes nitrogen purging and CO<sub>2</sub> adsorption. The adsorption capacity of CO<sub>2</sub> at a certain equilibrium concentration is calculated as Formula (S1). Amine efficiency is defined as the molar ratio of CO<sub>2</sub> adsorption capacity to amines (in terms of N), and the calculation equation is mentioned in Formula (S2).

#### 3. Results and discussion

#### 3.1. The synthesis of MOFs solid amine adsorbents via solvent effects

In Fig. 2(a), when MIL-100(Cr) was used as the carrier, the adsorption capacity and amine group utilization of MF-Cr-AEEA-H<sub>2</sub>O were found to be 0.51 mmol/g and 21.2 %, respectively, indicating poor adsorption performance. However, when CH<sub>3</sub>OH was used as the solvent, the adsorption capacity and amine group utilization of MF-Cr-AEEA-CH<sub>3</sub>OH increased significantly to 2.05 mmol/g and 85.4 %, respectively. Further improvement was observed when NMP was used as the solvent, resulting in an adsorption capacity of 2.15 mmol/g and an amine group utilization of 89.6 %. Similar trends in adsorption performance were observed for MIL-100(Fe) and UiO-66(Zr) solid amine adsorbents in different solvents, indicating that the solvent effect remained consistent across different MOFs, with the order of performance being NMP > CH<sub>3</sub>OH > H<sub>2</sub>O.

Fig. 2(b) shows the pH values of MIL-100(Cr), MIL-100(Fe), and UiO-66(Zr) slurry dispersed in different solvents. When  $H_2O$  was used as the solvent, the pH of MIL-100(Fe) and UiO-66(Zr) slurry was 1.51 and 2.20, respectively, which resulted in reduced effective grafting of amine groups, leading to a smaller adsorption capacity of 0.25 mmol/g and 0.06 mmol/g. On the other hand, the higher pH of MIL-100(Cr) slurry (3.45) improved the linking efficiency between Cr metal sites and amine groups, increasing the adsorption capacity to 0.51 mmol/g [19]. When CH<sub>3</sub>OH was used instead of H<sub>2</sub>O, the pH of MIL-100(Cr), MIL-100(Fe), and UiO-66(Zr) slurry increased to 4.05, 2.02, and 2.73, respectively. Importantly, With the use of NMP solvents, the pH of MOFs slurry is further increased. In detail, the pH of MIL-100(Fe) slurry increased to



**Fig. 2.** The adsorption performance of MOFs adsorbents prepared by different solvents (a) and the pH of MOFs slurry at different solvents. (Adsorption: temperature of 25 °C, CO<sub>2</sub> concentration of 400 ppm, water vapor concentration of 1 %; Desorption: temperature of 80 °C, time of 40 min).

3.54, and the pH of UiO-66(Zr) slurry increased to 3.62, further enhancing CO<sub>2</sub> adsorption capacity and amine group utilization. In particular, the adsorption capacity when using MIL-100(Fe) as the carrier increased significantly to 1.73 mmol/g, exhibiting a six-fold increase. And the adsorption capacity of UiO-66(Zr) increased significantly from 0.06 mmol/g to 1.71 mmol/g, representing a 27.5fold increase. Moreover, due to the lower acidity of MIL-100(Cr), the adsorbent using MIL-100(Cr) as the carrier in the same solvent exhibited higher adsorption capacity compared to that using MIL-100(Fe) or UiO-66(Zr) as the carrier [19].

The Fourier-transform infrared (FTIR) spectra of MF-Cr-AEEA prepared using different solvents (Fig. 3(a)) showed that the C-N stretching vibration band of primary amine groups was detected around 1170 cm<sup>-1</sup> in MF-Cr-AEEA, indicating the presence of active primary amine sites. However, the intensity of the C-N band of primary amine groups decreased significantly in MF-Cr-AEEA-H<sub>2</sub>O, while it remained strong in MF-Cr-AEEA-CH<sub>3</sub>OH and MF-Cr-AEEA-NMP, suggesting lower primary amine content in MF-Cr-AEEA-H<sub>2</sub>O and a poor grafting process when H<sub>2</sub>O was used as the solvent. Additionally, the bands at 2825 and 2930 cm<sup>-1</sup> corresponded to C-H vibration bands, and the characteristic asymmetric stretching absorption peak of carboxylic acid salts appeared at 1560  $\text{cm}^{-1}$  due to the MOFs ligand structure (Fig. S2). In addition, the specific surface area is also an important factor affecting the CO<sub>2</sub> capture ability of MOFs adsorbent materials. As displayed in Fig. 3(b), the illustrated isotherms for adsorbents using NMP as a solvent are assigned to a type IV pattern characteristic indicating that adsorbents were subjected to mesoporous materials. As depicted in Table 1, the specific surface area of MF-Cr-AEEA-NMP, MF-Fe-AEEA-NMP, and MF-Zr-AEEA-NMP were recorded as 3.53, 3.78, and 6.63  $m^2/g$ . The higher specific surface area of MF-Zr-AEEA-NMP than MF-Cr-AEEA-NMP and MF-Fe-AEEA-NMP enhances heat and mass transfer, which is beneficial to improve the adsorption kinetics. And, the surface morphology of the adsorbents using NMP as a solvent were characterized as shown in Fig. S3. The results showed that the surface morphology of all adsorbents resembled a spherical structure. Meanwhile, the forming structure of MF-Zr-AEEA-NMP is the best, with a diameter of about 0.2 µm. From the elemental analysis of the adsorbents using NMP as a solvent in Table S2, all the adsorbents had high N content, which proved the successful insertion of the amine active site.

Regarding the desorption data in Fig. 2(a), the desorption capacity of the adsorbents prepared with different solvent systems was over 90 %, indicating that the choice of solvent during the preparation process had minimal impact on the desorption properties. In addition, the semi-adsorption time for MF-Cr-AEEA-NMP, MF-Fe-AEEA-NMP, and MF-Zr-

#### Table 1

Specific surface area, average pore size, and pore volume of adsorbents using NMP as a solvent.

Adsorbents	Specific surface area (m <sup>2</sup> /g)	Average pore size (nm)	Pore volume (m <sup>3</sup> /g)
MF-Cr-AEEA- NMP	3.53	24.4	0.016
MF-Fe-AEEA- NMP	3.78	8.59	0.007
MF-Zr-AEEA- NMP	6.63	6.84	0.011

AEEA-NMP was recorded as 21, 15, and 14 min, respectively. These relatively short semi-adsorption times can be attributed to the high kinetic performance of the adsorbents. Meanwhile, due to the higher specific surface area of MF-Zr-AEEA-NMP than MF-Fe-AEEA-NMP and MF-Cr-AEEA-NMP, MF-Zr-AEEA-NMP owned the fastest adsorption rate. Moreover, in the practical application process, the cost problem is also an important factor affecting the large-scale use of adsorbents. The overall price of the solvent and adsorbent were analyzed in Table S3. Thereinto, due to the lack of cost data for large-scale MOFs preparation, the MOFs price in Table S3 is estimated according to the raw material price required for the laboratory preparation process, which is not include initial investment, labor, operations, etc. The solvent price is estimated according to the laboratory purchase price. From Table S3, MOFs type and solvent are the main contributors to the cost of adsorbent. Compared with UiO-66(Zr), the price of MIL-100(Cr) and MIL-100 (Fe) is lower, which is conducive to the reduction of the cost of adsorbent. Meanwhile, the choice of solvent can effectively control the cost of the adsorbent. In detail, the price of adsorbent using NMP as solvent is the most expensive, which is \$130-170/kg more expensive than the adsorbent using H<sub>2</sub>O as solvent.

# 3.2. The efficient response path of amine grafting process at different solvent systems

To further validate the experimental results, reveal grafting reaction paths of AEEA and MOFs at different solvent systems, and analyze the solvent effect for amine group utilization, the grafting reaction in three types of solvent systems was broadly discussed using the density functional theory (DFT). The grafting reaction in the three types of solvent systems was extensively studied, and a zwitterion-mediated two-step mechanism was proposed (Fig. 4) [11,19], including the interaction between the metal acid site of MOFs and secondary amine groups to



Fig. 3. FTIR spectra of MF-Cr-AEEA preparing by different solvents (a), Nitrogen adsorption-desorption isotherm of adsorbents using NMP as a solvent (b).



Fig. 4. Possible pathways and chemical reactions of amine grafting reaction. (M: the metal acid site of MOFs (Cr/Fe/Zr); B: the solvent in the amine grafting process; B<sup>⊖</sup>: the basic ion in the solvent (B)).

form a zwitterion and instantaneous deprotonation reaction by the base of solvent or primary amine (–NH<sub>2</sub>) of zwitterions. In this regard, MOFs with L acid sites first react with AEEA's secondary amine group to form zwitterions (*Reaction 1*) [19,27,28]. Then the zwitterion is instantaneously deprotonated by the basic ion ( $\mathbf{B}^{\Theta}$ ) in the solvent (**B**) (*Reaction* 2), leading to the activation of the adsorbent or by the primary amine (–NH<sub>2</sub>) of the zwitterion due to the influence of the solvent, which results in the inactivation of the adsorbent (*Reaction 3*). This reaction was also demonstrated because a major resonance around 160 ppm of carbamate chains (NHRCO<sub>2</sub>) from <sup>13</sup>C NMR spectra and a major carbon peak around 285.3 eV of carbon–nitrogen skeleton from C1s XPS spectrum were recorded of MF-Cr-AEEA after reaction with CO<sub>2</sub> in Fig. S4 [28,29]. The molecular simulation details of different solvent systems are shown in Figs. S5-S7.

As shown in Fig. **5(a)**, in the grafting activation reaction (*Reaction 2*) of MIL-100(Cr) and AEEA in different solvent systems, NMP exhibited

the lowest energy barrier of 385.34 kJ/mol and binding energy of -130.53 kJ/mol, indicating its excellent deprotonation ability and facilitating the formation of the adsorbent. On the other hand, H<sub>2</sub>O had the highest energy barrier, which was 24.16 kJ/mol higher than NMP, suggesting its weaker deprotonation ability compared to NMP. The results demonstrate that the presence of NMP as a solvent enhances the deprotonation step and promotes the formation of the adsorbent. During the adsorbent deactivation reaction (*Reaction 3*) of Fig. 5(b), the energy barrier of using NMP as solvent was 425.93 kJ/mol, higher than H<sub>2</sub>O and CH<sub>3</sub>OH. This indicates that the deactivation reaction is less likely to occur in the presence of NMP, further supporting the role of NMP in preventing the loss of active sites [30,31]. The binding energy of the deactivation reaction in the NMP system was also the lowest, reinforcing the trend of the deactivation reaction. Similar observations were made for the grafting reaction of MIL-100(Fe) and UiO-66(Zr) in different solvent systems, as depicted in Fig. S7.



Fig. 5. The binding energy and energy barrier at different solvent systems ((a) is *Reaction 2* of MIL-100 (Cr) grafting reaction, (b) is *Reaction 3* of MIL-100 (Cr) grafting reaction.

These results further confirmed the importance of aprotic solvents for effective deprotonation. Indeed, aprotic solvents facilitate the directed transfer of protons during the grafting process, leading to improved binding energies and reduced energy barriers for the deprotonation reaction. Moreover, when the solvent was changed from H<sub>2</sub>O to NMP, the CO<sub>2</sub> adsorption capacity increase rate of UiO-66(Zr) was the highest compared to MIL-100(Cr) and MIL-100(Fe).

In summary, a novel and more precise amine grafting reaction path was obtained by combining experiments with molecular simulations (Fig. 6). In this respect, the amine grafting process follows a zwitterionmediated two-step mechanism. The first reaction involves the interaction between the metal acid site of MOFs and secondary amine groups to form a zwitterion. Then, the zwitterion is instantaneously neutralized and deprotonated by the base ( $\mathbf{B}^{\Theta}$ ) of solvent or primary amine (-NH<sub>2</sub>) of zwitterion. Thus, the deprotonation is controlled by a two-part reaction pathway. Among these reactions, the solvent acts as a reactant that affects the process of grafting reaction in **Path 1**. In **Path 2**, the solvent acts as a transport carrier of  $H^+$ , influencing the reaction energy barrier, while the primary amine that received the H<sup>+</sup> ion loses its ability to adsorb CO<sub>2</sub>. Importantly, the choice of solvent can regulate proton migration by influencing the binding energy and energy barrier of the deprotonation reaction, thereby further targeting and regulating the deprotonation process. Notably, aprotic solvents facilitate proton transfer during grafting and optimize the binding energy of the deprotonation reaction, resulting in an improved adsorption capacity.

# 3.3. Optimize of regeneration energy consumption for MOFs solid amine adsorbents

According to the comparative analysis of adsorbent cost and adsorption capacity in section 3.1, MF-Cr-AEEA-CH<sub>3</sub>OH can meet the requirements of high adsorption capacity at a relatively low cost, which is the more potential adsorbent. So, based on the experiments and calculations, the regeneration energy of MF-Cr-AEEA-CH<sub>3</sub>OH was analyzed via differential scanning calorimetry to optimize the energy consumption of the adsorbent. As shown in Table 2, the regeneration energy consumption for a solid amine adsorbent can be provided as the sum of the heat of adsorption ( $\Delta H_{ads}$ ), the latent heat of vaporization of adsorbed water (E<sub>H2O</sub>), which is typically large, and the sensible heat for

Table 2

Regeneration energy consumption composition of MF-Cr-AEEA when adsorption temperature is 25  $^\circ C$ , and desorption temperature is 80  $^\circ C$ .

Composition	Dry conditions	$\begin{array}{l} RH=30\\ \%\end{array}$	$\begin{array}{c} RH = 60 \\ \% \end{array}$	Saturation humidity
q <sub>CO2</sub> (mol/kg)	1.45	2.05	2.08	1.90
q <sub>H2O</sub> (mol/kg)	0.00	1.92	4.74	15.93
$\Delta H_{ads}$ (GJ/t	1.20	1.20	1.20	1.20
CO <sub>2</sub> )				
E <sub>H2O</sub> (GJ/t CO <sub>2</sub> )	0.00	0.88	2.18	7.34
Esen (GJ/t CO <sub>2</sub> )	1.28	1.28	1.28	1.28
$E_{tot}$ (GJ/t CO <sub>2</sub> )	2.48	3.28	4.66	9.82

heating the sorbent from the adsorption to the desorption temperature  $(E_{sen})$  [15,32,33].

The  $\Delta H_{ads}$  refers to the energy released by capturing CO<sub>2</sub> at the active site of the adsorbent. It includes heat of physical adsorption and heat of chemical adsorption. From Fig. S8, the adsorption heat of MF-Cr-AEEA was analyzed via differential scanning calorimetry in a CO2 atmosphere (adsorption temperature of 25 °C and adsorption time of 140 min). An exothermic heat flow of 108.03 J/g was observed at an adsorption time of 160 min. When this heat flow was correlated to the adsorption experiment capacity under similar conditions, an approximate, average  $\Delta H_{ads}$  of 1.20 GJ/t CO<sub>2</sub> was calculated, which is about 15 % less than that of MIL-101(Cr)-TEPA reported in the literature [33]. The low  $\Delta H_{ads}$  can be attributed to the mechanism of spontaneous cooling adsorption of the MF-Cr-AEEA adsorbent (Fig. S9) [34]. In detail, the entropy increase ( $\Delta S$ ) of the adsorption process dominated the heat of CO<sub>2</sub> adsorption [34]. From the optimized molecular structures of the hydrated ion pairs by density functional theory (DFT) (Fig. 7 (a) and Fig. S10), in the case of MF-Cr-AEEA, water molecules are uniformly located around the anion, while the water molecules selfassociated or form clusters in the case of carbamic acid. It is due to the loss of the hydrophilic sites of the secondary amine group in its coordination with the metal site, while the hydrophilic sites of the primary amine group also decrease after the adsorption of CO<sub>2</sub>. The unique amine grafting method increases the hydrophobicity of CO<sub>2</sub> adsorption products. And the modified hydrophobicity results in a significant increase in the  $\Delta S$  of the hydrated ion pairs after the adsorption reaction



Fig. 6. Grafting reaction path diagram of MOFs grafting reaction in different solvent systems.



**Fig. 7.** The entropy change of spontaneous cooling adsorption at different relative humidity levels (a) and the  $H_2O$  adsorption capacity of MIL-100(Cr), MF-Cr-AEEA and other  $CO_2$  adsorbents at different relative humidity levels (b). (blue: nitrogen atoms, gray: carbon atoms, red: oxygen atoms, white: hydrogen atoms). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Fig. 7(a)), which effectively reduces the heat of CO<sub>2</sub> adsorption [34].

The E<sub>H2O</sub> is mainly dominated by the water adsorption capacity of the adsorbent. In theory, the smaller the amount of water adsorbed, the lower the latent heat required. From Fig. 7(b), after grafting AEEA, the H<sub>2</sub>O adsorption of MF-Cr-AEEA adsorbent was 19.53 mmol/g under saturated humidity, which is 46 % lower than that of MIL-100(Cr). When RH = 70 %, the H<sub>2</sub>O adsorption capacity was also significantly lower than that of MIL-101(Cr)-TEPA and Al2O3-TEPA reported in the literature [33], which is due to the decreased of carrier water adsorption site after grafting AEEA [35-37]. Meanwhile, the hydrophobicity of AEEA than TEPA is also conducive to promoting the decrease of water adsorption of the MF-Cr-AEEA. Based on the water molecular adsorption data of DFT combined with the water adsorption capacity experiment, it can be seen that the water adsorption of the MF-Cr-AEEA tends to change in the direction of hydrophobic, which is conducive to the reduction of regeneration energy consumption. In addition, the  $E_{\rm H2O}$  is also closely related to the condition of adsorption/desorption process and the performance of adsorbent (Figs. S11-S13). In detail, high CO<sub>2</sub> adsorption capacity and the amine group utilization are conducive to reducing regeneration energy consumption.

Approximate heat capacities ( $C_P$ ) of MF-Cr-AEEA were characterized by Differential Scanning Calorimeter to analyze the E<sub>sen</sub> of MF-Cr-AEEA. As shown as Fig. S14, because of the insertion of the AEEA, the specific heat capacity of MF-Cr-AEEA is significantly greater than that of MIL-100(Cr). Over the 80 °C temperature range, the average heat required to regenerate CO<sub>2</sub>-loaded MF-Cr-AEEA was only 2.1 J/g-K. For comparison, the heat capacity of a 30 wt% AEEA solution without CO<sub>2</sub> is around 2.9 J/g-K over the same 80 °C range, proving the excellent heat and mass transfer performance of the MF-Cr-AEEA [38,39]. In addition, the significantly greater adsorption capacity of MF-Cr-AEEA means that a smaller mass is required to adsorb the same amount of CO<sub>2</sub>, which reduces the sensible heat required.

Based on the data of  $\Delta H_{ads}$ ,  $E_{H2O}$  and  $E_{sen}$ , the regeneration energy consumption of the MF-Cr-AEEA is around 2.48–9.82 GJ/t CO<sub>2</sub> when adsorption temperature is 25 °C and desorption temperature is 80 °C (Table 2). Thereinto, the regeneration energy consumption would be approximately 2.48 GJ/t CO<sub>2</sub> under dry adsorption conditions. And this value also compares very favorably with the 4.02–4.86 GJ of energy necessary to release 1 t of CO<sub>2</sub> from the absorbent solution [40,41]. Moreover, compared with other solid amine DAC adsorbents reported in the literature (Fig. 8), the regeneration energy consumption decreased significantly demonstrating outstanding industrial applications potential of the adsorbent.



Fig. 8. Comparison of regeneration energy consumption between MF-Cr-AEEA and other CO<sub>2</sub> adsorbents [33,36,42].

#### 4. Conclusions

In this study, to improve the amine grafting efficiency and reduce the energy consumption of DAC technology, we prepared aminefunctionalized MIL-100(Cr), MIL-100(Fe), and UiO-66(Zr) by directional deprotonation regulation of MOFs-based amine grafting. The results showed that the organic polar aprotic solvents can release the active site of the amine group and make it refix carbon, further improving its adsorption capacity and amine group utilization. In detail, an ultra-high CO<sub>2</sub> adsorption capacity of 2.15 mmol/g and amine group utilization of 89.6 % at ambient conditions were obtained when using NMP as solvent to prepare a MIL-100(Cr)-based DAC adsorbent. And the CO2 adsorption performance of the UiO-66(Zr)-based adsorbent significantly increased from 0.06 mmol/g of using H2O as solvent to 1.71 mmol/g of using NMP, with a 27.5-fold increase. To reveal the efficient response path of grafting process at different solvent systems, three types of solvent systems were broadly discussed using the density functional theory (DFT). The molecular simulations revealed that solvents act as reactants to improve the grafting process and serve as transport carriers for H<sup>+</sup> ions to the primary amine group, potentially leading to a loss of CO<sub>2</sub> adsorption ability. Furthermore, the regeneration energy consumption of the MF-Cr-AEEA was analyzed via the calculation of  $\Delta H_{ads}, E_{H2O}$  and  $E_{sen}$ , to optimize the energy consumption of the adsorbent. The results indicate that the regeneration heat is mainly determined by the amount of water adsorbed by the MF-Cr-AEEA. Due to the hydrophobicity of the CO<sub>2</sub> adsorption products, which increased the  $\Delta$ S of adsorption process and further reduced the heat of CO<sub>2</sub> adsorption. Based on changes in humidity conditions, the regeneration energy consumption would be approximately 2.48–9.82 GJ/t CO<sub>2</sub> demonstrating outstanding industrial applications potential of the adsorbent.

#### CRediT authorship contribution statement

Tao Wang: Writing – review & editing, Resources, Funding acquisition, Conceptualization. Fengsheng Liu: Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. Wenjing Tang: Writing – review & editing, Methodology. Shisen Xu: Writing – review & editing, Methodology, Conceptualization. Hao Dong: Writing – review & editing, Methodology. Zhijie Chen: Writing – review & editing, Software, Resources. Xiang Gao: Writing – review & editing, Software, Resources, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

The data supporting the findings of this study are available within the paper and its <u>Supplementary Information</u> files. Raw data are available from the corresponding author on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2024.151426.

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