

# Polyethyleneimine-Modified Amorphous Silica for the Selective Adsorption of CO<sub>2</sub>/N<sub>2</sub> at High Temperatures

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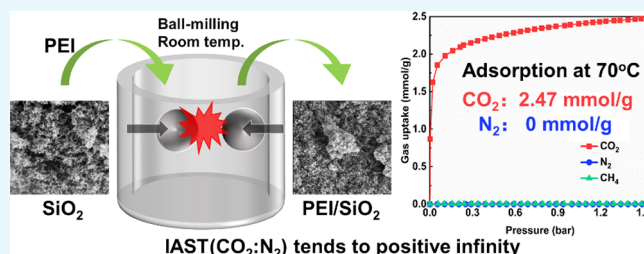
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**ABSTRACT:** Mechanochemistry is very attractive as an efficient, solvent-free, and simplified technique for the preparation of composite adsorbents. Here, a series of polyethyleneimine (PEI)-modified SiO<sub>2</sub> adsorbents were prepared via mechanical ball milling for selective adsorption of CO<sub>2</sub> at high temperatures. The structural properties of these adsorbents were characterized by XRD, SEM, TGA, FTIR, and N<sub>2</sub> adsorption–desorption. This method can better disperse the PEI evenly in the SiO<sub>2</sub> as well as maintain the porous structure of the adsorbents by comparing with the impregnated adsorbents. These adsorbents presented appreciable performance in separating CO<sub>2</sub> at high temperatures, and the CO<sub>2</sub> adsorption capacity of PEI(70%)/SiO<sub>2</sub> is up to 2.47 mmol/g at 70 °C and 1.5 bar, which is significantly higher than that of the same type of CO<sub>2</sub> adsorbent reported in the literature. Furthermore, the adsorbent of PEI(70%)/SiO<sub>2</sub> provided an ideally infinite selectivity for CO<sub>2</sub>/N<sub>2</sub> (15:85) at 70 °C. These results showed that mechanical grinding methods are a simple and effective approach to producing amine-modified silica composite adsorbents.



## 1. INTRODUCTION

Atmospheric CO<sub>2</sub> is continuously increasing at a high rate, which is mainly due to the intensive use of fossil fuels.<sup>1</sup> Further, the environmental issue caused by the increase in CO<sub>2</sub> has become a global problem that cannot be ignored.<sup>2,3</sup> Many options for reducing CO<sub>2</sub> emissions had been investigated and liquid amine adsorption was generally considered to be one of the most effective methods of CO<sub>2</sub> capture.<sup>4,5</sup> However, this method has some disadvantages such as high cost, high energy consumption, amine losses, and high corrosiveness. These issues limit the potential of liquid amines for CO<sub>2</sub> capture applications.<sup>6,7</sup>

There has been a great concern for the development of efficient solid adsorbents for the capture of CO<sub>2</sub>. Particularly, it is of high significance for the capture of high-temperature flue gases in thermal power plants (CO<sub>2</sub>/N<sub>2</sub> of about 0.15/0.85).<sup>8</sup> Solid amine adsorbents have the advantage of both physisorption and chemisorption, which makes them one of the most promising methods for capturing CO<sub>2</sub>.<sup>8,9</sup> Therefore, many porous materials are widely used as an amine support for the physical and chemical adsorption of CO<sub>2</sub>, including porous carbon,<sup>10,11</sup> mesoporous silica,<sup>12–14</sup> zeolites,<sup>15,16</sup> porous polymers,<sup>17,18</sup> and metal–organic frameworks (MOFs).<sup>19,20</sup> As mentioned above, mesoporous silica is widely used as a support to immobilize amines due to its good thermal stability, high pore volume, and abundance of surface silica hydroxyl groups.<sup>9,21,22</sup>

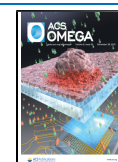
There are two main approaches to preparing solid amine adsorbents: (a) wet impregnation and (b) silane chemis-

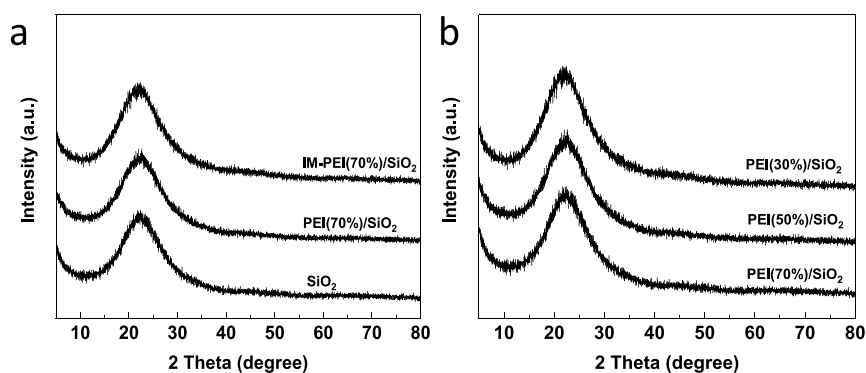
try.<sup>8,13,23–25</sup> Wet impregnation is a simple and most common technique for the addition of organic amines to mesoporous silica. Nevertheless, these methods require large amounts of solution and long synthesis times. In addition, the removal of the solvent also requires energy, which has a significant impact on production costs. In the case of the industrial synthesis of solid amine adsorbents and protection of the environment, mechanochemistry could be used as a simple, efficient, and sustainable method.<sup>26,27</sup> The mechanochemical method has the obvious effect of changing the physicochemical properties of the materials, i.e., changing the size of the particles, creating structural defects, enhancing the chemical reactions during the grinding process, etc.<sup>27–32</sup> There have been reports of condensation reactions between hydroxyl groups on the surface of silica and siloxane groups by mechanochemical methods.<sup>32,33</sup> Amrute *et al.*<sup>33</sup> reported the mechanochemical functionalization of different supports (SBA-15, SiO<sub>2</sub> gel, etc.) with various silicone compounds without the use of any solvent in only 5 min at room temperature, which provides a new idea for the modification of silica with organic amines.

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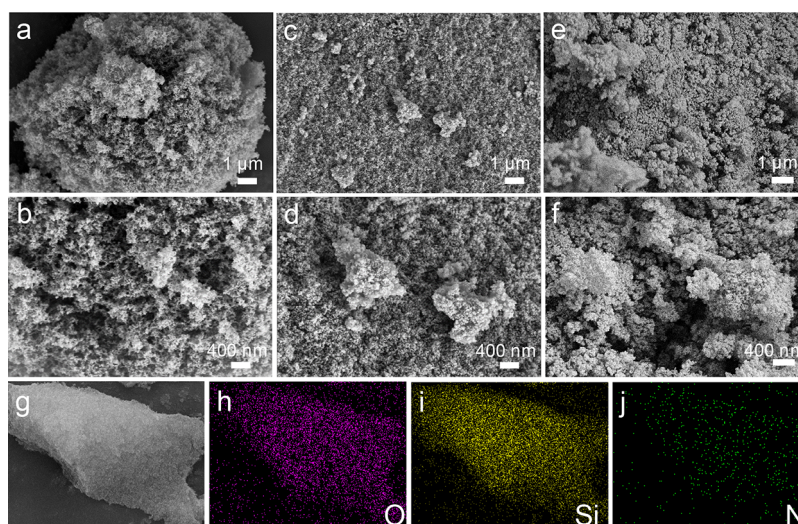
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**Figure 1.** XRD patterns of (a)  $\text{SiO}_2$  before and after PEI modification and (b) different loading amounts of PEI-modified  $\text{SiO}_2$ .



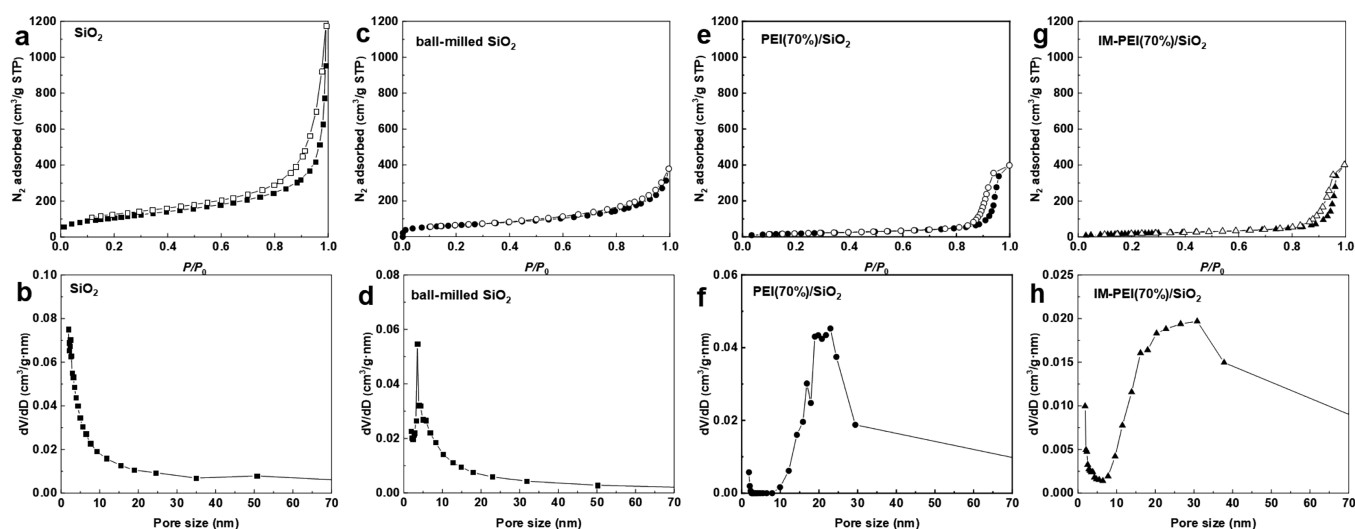
**Figure 2.** SEM images of (a, b) silica, (c, d) PEI(70%)/ $\text{SiO}_2$ , and (e, f) IM-PEI(70%)/ $\text{SiO}_2$ . (g–j) Elemental (O, Si, and N) mapping images of PEI(70%)/ $\text{SiO}_2$ .

Polyethyleneimine (PEI) has high  $\text{CO}_2$  absorption capacity, which is used as a modifier to modify silica for improving  $\text{CO}_2$  adsorption performance and selectivity.<sup>8,34–37</sup> The most commonly used method for constructing amine-silica adsorbents is the solvent impregnation method, in which amine can be uniformly dispersed on the silica. However, the silica with high amine loading is easy to agglomerate, and the use of organic solvents for dispersion also increases the production cost. Therefore, it is highly desirable to develop an effective method to prepare high amine loading silica adsorbents for effective separation of  $\text{CO}_2$ . Herein, we demonstrated a straightforward method to prepare a silica adsorbent with high PEI loading by the mechanical grinding method without any solvents. The structural properties of adsorbents synthesized using different methods were systematically characterized by XRD, SEM, TGA, FTIR, and  $\text{N}_2$  adsorption–desorption. The  $\text{CO}_2$  adsorption performance of adsorbents was investigated, and the adsorption selectivity of  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$  binary mixtures was also calculated from the ideal adsorbed solution theory (IAST). In addition, the  $\text{CO}_2$  adsorption isotherms and the isosteric heats of  $\text{CO}_2$  adsorption were discussed by the dual-site Langmuir–Freundlich (DSLFF) model and Clausius–Clapeyron equation.

## 2. RESULTS AND DISCUSSION

**2.1. Characterization of PEI-Modified  $\text{SiO}_2$  Adsorbents.** The PEI-modified  $\text{SiO}_2$  adsorbents were prepared by impregnation and ball milling methods, and the obtained adsorbents were marked as IM-PEI(70%)/ $\text{SiO}_2$  and PEI(70%)/ $\text{SiO}_2$ , respectively, where 70% represents the mass fraction of PEI. The structure of the PEI-modified  $\text{SiO}_2$  adsorbents was characterized by XRD. As shown in Figure 1a, a broadened peak from  $2\theta$  of  $10^\circ$  to  $35^\circ$  corresponds to the amorphous silica phase.<sup>38</sup> The crystalline structure of silica did not change after 70% PEI was loaded by either the impregnation method or ball milling method. In addition, changing the loading amount of PEI has no significant effect on the crystal structure of silica (Figure 1b). It is suggested that PEI was fixed on silica through physical interaction.

The microstructure of adsorbents was studied by SEM, and results are shown in Figure 2.  $\text{SiO}_2$  has a rich porous structure and is very favorable for supporting amine (Figure 2a,b). The surface texture of the amine-modified silica became denser after supporting 70% PEI. The pores of  $\text{SiO}_2$  also significantly reduced, indicating that PEI was uniformly loaded on the support due to the strong interaction of mechanical grinding (Figure 2c,d). Furthermore, elemental mapping images of Figure 2g show uniform dispersions of N throughout the support  $\text{SiO}_2$ , thus indicating that the PEI units are uniformly dispersed in the adsorbent. In contrast, the agglomeration of



**Figure 3.**  $N_2$  adsorption–desorption isotherms and BJH pore size distributions of (a, b)  $SiO_2$ , (c, d) ball-milled  $SiO_2$ , (e, f) PEI(70%)/ $SiO_2$ , and (g, h) IM-PEI(70%)/ $SiO_2$ .

IM-PEI(70%)/ $SiO_2$  prepared by the impregnation method is easier. Large pore channels were also obtained by removing the solvent from the adsorbent during the impregnation synthesis (Figure 2e,f).

The  $N_2$  adsorption/desorption isotherms and BJH pore size distribution curves of  $SiO_2$  and PEI-modified  $SiO_2$  adsorbents are drawn in Figure 3. After directly ball-milling  $SiO_2$ , the specific surface area of ball-milled  $SiO_2$  decreases observably, indicating excessive collapse of the pore structure. This was due to the absence of protective agents (e.g., PEI and ethanol) during ball milling.<sup>39,40</sup> The specific surface area of  $SiO_2$  was further reduced by loading different masses of PEI, and all PEI-modified  $SiO_2$  adsorbents exhibit almost classic type IV isotherms.<sup>41</sup> Notably, PEI(70%)/ $SiO_2$  exhibits a prominent type H3 hysteresis, indicating the presence of mesopores. Even if the loading of PEI is augmented, there is still no significant change in hysteresis loops of PEI(70%)/ $SiO_2$  (Figure S1). In contrast, the hysteresis loops of IM-PEI(70%)/ $SiO_2$  shift from type H3 to type H1 with the increase in PEI loading.<sup>42,43</sup> Furthermore, the BJH pore size distribution curves indicate that modified adsorbents prepared by mechanical grinding have narrower aperture distribution. This narrower pore size is conducive to the adsorption and mass transfer of  $CO_2$ . As shown in Table 1, the  $S_{BET}$  of all the PEI-modified  $SiO_2$

adsorbents decreases with the increase in PEI loading, which is in line with expectations. According to the pore structure information of the PEI-modified  $SiO_2$  adsorbents prepared by the ball milling method and impregnation method, both methods are effective for loading amines onto  $SiO_2$ . From the perspective of environmental-friendliness, the ball milling method has more advantages because it can achieve a uniform load of a large amount of PEI and maintain the porosity of the adsorbent to a certain extent.

The thermostability of PEI-modified  $SiO_2$  was analyzed by TGA analysis.<sup>14,42,44</sup> As shown in Figure 4a, the initial weight loss below 125 °C was attributed to desorption of water,  $CO_2$ , and other volatile gases. As shown in Figure 4b, IM-PEI(70%)/ $SiO_2$  had a further mass loss (about 4%) in the temperature range of 150 to 230 °C, while no weight loss was observed in PEI (70%)/ $SiO_2$ . It indicated that the adsorbent prepared by mechanical ball milling is more thermally stable. Furthermore, the dramatic weight loss after 230 °C shows the significant loss of PEI. This is mainly due to the decomposition of the amino group. In summary, the TGA results show the good thermal stability of ball-milled adsorbents.

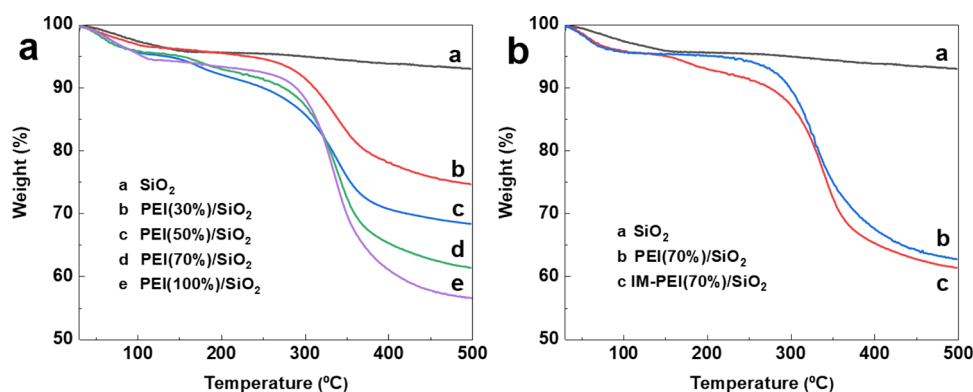
The FTIR spectra of the adsorbents are shown in Figure 5. The corresponding functional groups of  $SiO_2$  are indicated in Figure 5a. The peaks at 3750–3400  $cm^{-1}$  and 967  $cm^{-1}$  are attributed to O–H vibrations of the silica surface. After PEI modification, peaks at 1643 and 1573  $cm^{-1}$  correspond to the vibrations of secondary amine ( $R_2NH$ ) and primary amine ( $RNH_2$ ), respectively.<sup>8</sup> The chemical structure of PEI chains was also observed at 2957 and 2836  $cm^{-1}$ . The adsorbents synthesized by the impregnated method also show a similar characteristic infrared absorption peak (Figure S2). Therefore, these PEI-modified  $SiO_2$  adsorbents can chemically adsorb  $CO_2$ .<sup>45</sup> Notably, it is worth noting that for the characterization of PEI(70%)/ $SiO_2$  after adsorbing a large amount of  $CO_2$ , physically adsorbed  $CO_2$  could be clearly identified at 2340  $cm^{-1}$  (Figure 5b).<sup>22</sup> The above results indicate that  $CO_2$  can be adsorbed through synergistic physical and chemical adsorption.

**2.2.  $CO_2$  Adsorption.** The influence of the PEI loads and different synthesis methods on the  $CO_2$  adsorption capacity at 25 °C was studied, and results are shown in Figure 6. For both the mechanical grinding and impregnation methods, the  $CO_2$

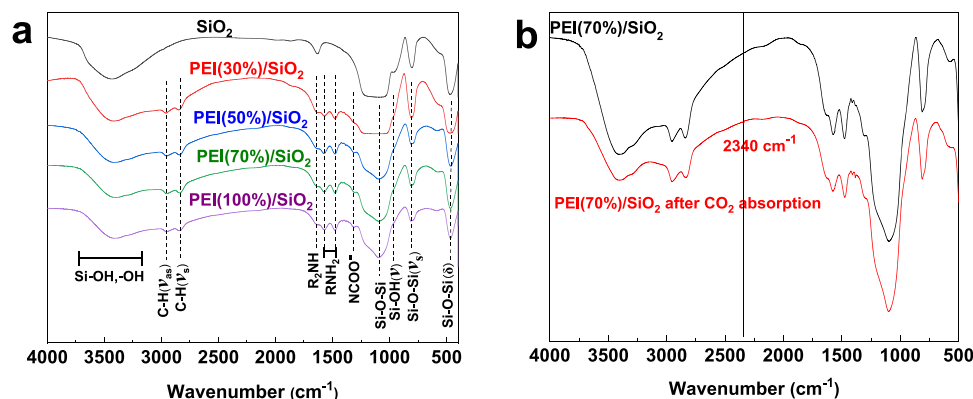
**Table 1.** Textural Properties of the Synthesized Adsorbents

sample	$S_{BET}$ ( $m^2/g$ )	$V_{BJH}^a$ ( $cm^3/g$ )	$d_{BJH}^b$ (nm)	$CO_2$ uptake <sup>c</sup>
$SiO_2$	393.28	1.59	14.51	0.59
ball-milled $SiO_2$	223.71	0.55	8.91	
PEI(30%)/ $SiO_2$	122.32	0.56	10.04	1.21
PEI(50%)/ $SiO_2$	100.14	0.53	11.91	1.54
PEI(70%)/ $SiO_2$	70.86	0.63	20.06	1.80
PEI(100%)/ $SiO_2$	55.84	0.51	19.33	1.67
IM-PEI(30%)/ $SiO_2$	118.91	1.46	26.95	1.29
IM-PEI(50%)/ $SiO_2$	81.46	1.10	27.08	1.66
IM-PEI(70%)/ $SiO_2$	72.37	0.63	19.89	1.70
IM-PEI(100%)/ $SiO_2$	19.85	0.24	22.83	1.06

<sup>a</sup>Cumulative BJH desorption pore volume. <sup>b</sup>Average BJH desorption pore diameter. <sup>c</sup>Adsorption capacity of  $CO_2$  at 25 °C (1.0 bar).



**Figure 4.** (a) TGA curves of the PEI-modified SiO<sub>2</sub> adsorbents prepared by the ball milling method with different PEI loads and (b) PEI(70%)/SiO<sub>2</sub> vs IM-PEI(70%)/SiO<sub>2</sub>.



**Figure 5.** (a) FTIR spectra of the silica adsorbent prepared by ball milling with different PEI loads and (b) FTIR spectra of PEI(70%)/SiO<sub>2</sub> before and after adsorption of CO<sub>2</sub>.

adsorption capacity of PEI-modified SiO<sub>2</sub> increases with increasing amine content (Figure 6a,b). When the mass ratio of PEI to SiO<sub>2</sub> was 0.7:1, the CO<sub>2</sub> adsorption capacity of the adsorbents synthesized by both methods reached maximum values. The CO<sub>2</sub> adsorption capacity of PEI(70%)/SiO<sub>2</sub> is 1.88 mmol/g at 1.5 bar and 25 °C. However, the CO<sub>2</sub> adsorption capacity of the impregnated adsorbents decreased sharply with further increasing PEI load. That is a result of blocking in the silica pores and the amine covering the SiO<sub>2</sub> surface in caking form, which prevents CO<sub>2</sub> molecules from entering the active center of adsorption and leads to an obvious reduction in CO<sub>2</sub> adsorption capacity.<sup>42,46</sup> Furthermore, PEI(70%)/SiO<sub>2</sub> has a faster CO<sub>2</sub> adsorption rate (Figure S3), which may be due to the better retention of the pores of PEI(70%)/SiO<sub>2</sub> than IM-PEI(70%)/SiO<sub>2</sub>. These all suggest that mechanical grinding is a promising way to prepare amine-modified adsorbents.

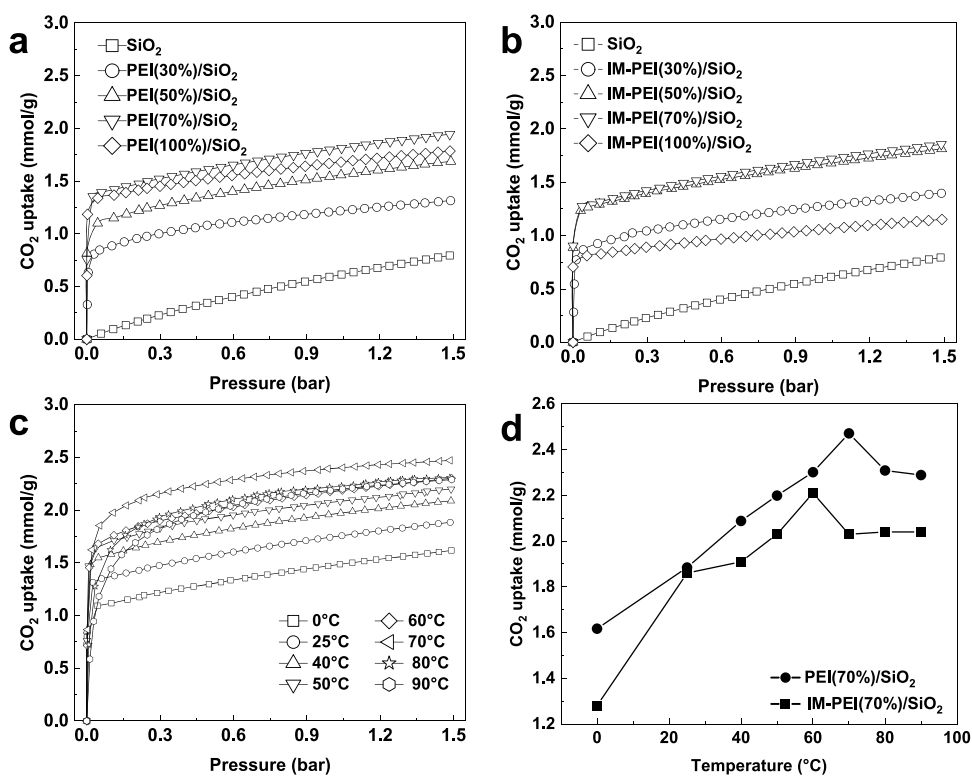
The CO<sub>2</sub> adsorption by PEI-modified SiO<sub>2</sub> adsorbents was further investigated at temperatures ranging from 0 to 90 °C, as shown in Figure 6c. A high temperature is unfavorable for CO<sub>2</sub> adsorption, but the viscosity of PEI and the diffusion resistance of CO<sub>2</sub> in the inner layer are reduced.<sup>8</sup> Therefore, more amine sites are exposed, enabling enhanced CO<sub>2</sub> adsorption with increasing temperature. The adsorption capacity reached a maximum of 2.47 mmol/g at 70 °C and 1.5 bar. Then, CO<sub>2</sub> adsorption decreased with further temperature increase but still maintained a high capacity. More importantly, CO<sub>2</sub> uptake is already up to 1.95 mmol/g at 70 °C and 0.15 bar, indicating the effective adsorption of low-pressure CO<sub>2</sub> by PEI(70%)/SiO<sub>2</sub>. The adsorption performance

of IM-PEI(70%)/SiO<sub>2</sub> for CO<sub>2</sub> was also tested under the same conditions (Figure S4). It is found that the PEI-modified SiO<sub>2</sub> adsorbent prepared by the ball milling method has a higher adsorption capacity (Figure 6d) and speculated that the ball milling method has a higher amine utilization rate than the impregnation method.

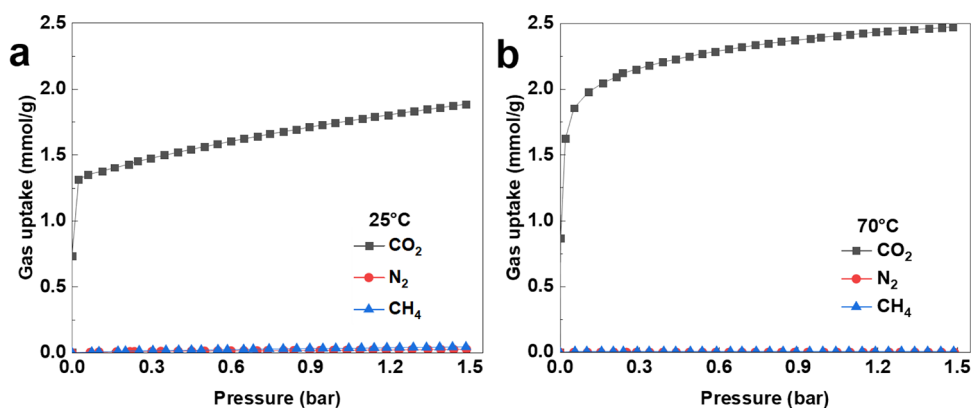
**2.3. N<sub>2</sub> and CH<sub>4</sub> Adsorption.** We also investigated the N<sub>2</sub> and CH<sub>4</sub> adsorption of the material. As shown in Figure 7, the isotherms of CH<sub>4</sub> and N<sub>2</sub> were significantly different from the shape of the CO<sub>2</sub> isotherm. CO<sub>2</sub> adsorption is a combined adsorption through physical and chemical interactions. In contrast, the N<sub>2</sub> and CH<sub>4</sub> isotherms are almost linear, indicating that the adsorption is physisorption and adsorbents lack specific adsorption sites for N<sub>2</sub> and CH<sub>4</sub>. As shown in Figure S5, even at 0 °C and 1.5 bar, the adsorption of N<sub>2</sub> (0.037 mmol/g) and CH<sub>4</sub> (0.086 mmol/g) was very low. These results showed that adsorbents have a strong affinity for CO<sub>2</sub>. Interestingly, the adsorbent showed no uptake of N<sub>2</sub> at 70 °C, demonstrating that the adsorbent could completely separate CO<sub>2</sub> and N<sub>2</sub> at 70 °C.

**2.4. Selectivity and Isothermic Heat of Adsorption.** In this work, we have calculated the gas selectivity of PEI(70%)/SiO<sub>2</sub> by IAST. At first, the DSLF equation was employed to fit the adsorption isotherms for CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>, as expressed by:<sup>19</sup>

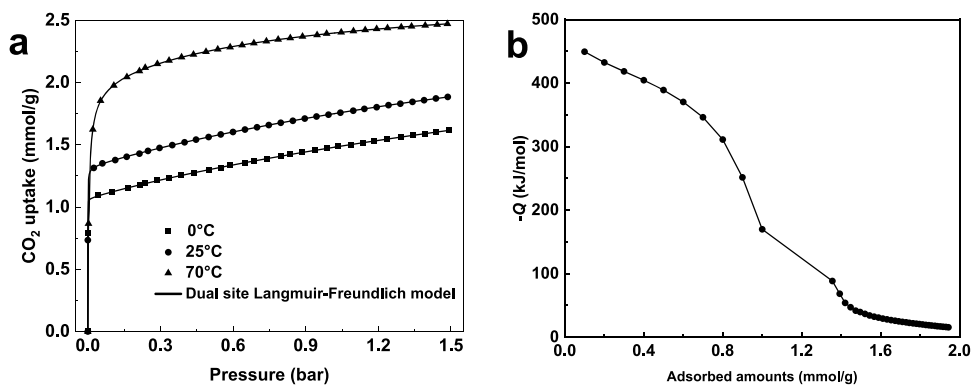
$$q = \frac{q_1 b_1 p^{1/n_1}}{1 + b_1 p^{1/n_1}} + \frac{q_2 b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}} \quad (1)$$



**Figure 6.** CO<sub>2</sub> absorption isotherms of (a) ball-milled PEI-modified adsorbents and (b) PEI-impregnated adsorbents at 25 °C. (c) CO<sub>2</sub> absorption isotherms of PEI(70%)/SiO<sub>2</sub> at different temperatures. (d) CO<sub>2</sub> absorption trends for PEI(70%)/SiO<sub>2</sub> and IM-PEI(70%)/SiO<sub>2</sub> at different temperatures.



**Figure 7.** CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> absorption isotherms of PEI(70%)/SiO<sub>2</sub> at (a) 25 °C and (b) 70 °C.



**Figure 8.** (a) CO<sub>2</sub> adsorption isotherms and dual-site Langmuir–Freundlich model fits for PEI(70%)/SiO<sub>2</sub> at 0, 25, and 70 °C. (b) Isosteric heat of adsorption for CO<sub>2</sub> on PEI(70%)/SiO<sub>2</sub> according to the CO<sub>2</sub> adsorption data at 0 and 25 °C.

where  $q$  is the equilibrium absorption (mmol/g) at gas pressure  $p$  (bar),  $q_i$  is the capacity of sites  $i$  (mmol/g) at saturation,  $b_i$  is the affinity coefficients of sites  $i$ , and  $n_i$  is the ideal homogeneous surface deviation. The fitting parameters for the DSLF model are listed in Table S1, and Figure 8a shows the experimentally CO<sub>2</sub> adsorption isotherms and model curves. The results indicated that the model gives a good fit to the experimental isotherms of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. Then, the adsorption isotherms of the gas mixture were predicted by IAST and the selectivity of the binary gas mixture was calculated. The equation is shown as:<sup>48</sup>

$$S = \frac{x_1/x_2}{y_1/y_2} \quad (2)$$

where  $x$  is the molar fraction in the adsorbed phase and  $y$  is the molar fraction in the gas phase. At 25 °C and 1 bar, the selectivity values of PEI(70%)/SiO<sub>2</sub> for CO<sub>2</sub>/N<sub>2</sub> (15:85) and CO<sub>2</sub>/CH<sub>4</sub> (40:60) binary gas mixtures were 561.0 and 148.5, respectively. Moreover, PEI(70%)/SiO<sub>2</sub> exhibits a high CO<sub>2</sub> adsorption capacity as well as high CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivity at low CO<sub>2</sub> pressure and 70 °C. As shown in Table 2, the selectivity of PEI(70%)/SiO<sub>2</sub> is higher than that of many

**Table 2. Comparison of Selectivity for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> Mixtures**

adsorbent	T (°C)	CO <sub>2</sub> uptake <sup>d</sup>	S <sub>CO<sub>2</sub>/N<sub>2</sub></sub>	S <sub>CO<sub>2</sub>/CH<sub>4</sub></sub>	ref
PEI(70%)/SiO <sub>2</sub> <sup>a</sup>	25	1.40	561.0	148.5	this work
PEI(70%)/SiO <sub>2</sub> <sup>a</sup>	70	2.04	infinite <sup>e</sup>	148.5	
MCM-41 <sup>b</sup>	25		11		47
TRI-PE-MCM-41 <sup>b</sup>	25		308 <sup>f</sup>		47
MOF-505@5GO <sup>a</sup>	25	1.25	37.2	8.6	19
C-COP-P-Mn <sup>c</sup>	25	0.13		6.3	48
PAN-NP <sup>c</sup>	0	0.80	101.1	16.5	49
nanosized zeolite L <sup>a</sup>	25	1.96	198.6	75.3	50
cylindrical zeolite <sup>a</sup>	25	1.65	188.6	72.9	50
NPC-3-500 <sup>a</sup>	0	1.39	160.4		51

<sup>a</sup>The gas mixtures of CO<sub>2</sub>/N<sub>2</sub> (15:85) and CO<sub>2</sub>/CH<sub>4</sub> (40:60) at 1 bar. <sup>b</sup>The gas mixtures of CO<sub>2</sub>/N<sub>2</sub> (20:80) at 1 bar. <sup>c</sup>The gas mixtures of CO<sub>2</sub>/N<sub>2</sub> (15:85) and CO<sub>2</sub>/CH<sub>4</sub> (50:50) at 1 bar. <sup>d</sup>CO<sub>2</sub> uptake at 0.15 bar CO<sub>2</sub> (mmol/g). <sup>e</sup>The adsorbent showed no uptake of N<sub>2</sub> at 70 °C; thus, the adsorbents showed ideally infinite selectivity. <sup>f</sup>CO<sub>2</sub>/N<sub>2</sub> molar selectivity ratio for materials at 1 bar.

reported porous materials. It is a promising CO<sub>2</sub> capture adsorbent especially for the separation of high-temperature flue gas.

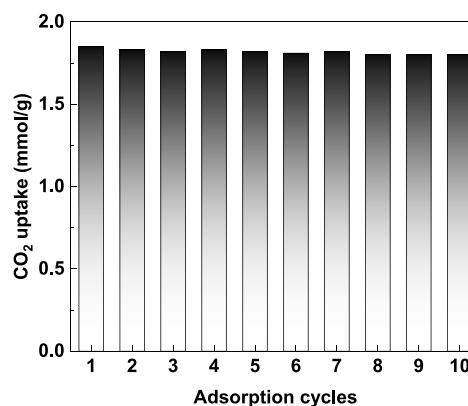
The isotropic heat of adsorption ( $Q_{st}$ ) was calculated from the CO<sub>2</sub> adsorption data at 0 and 25 °C using the Clausius–Clapton equation:<sup>17</sup>

$$Q_{st} = \frac{RT_1T_2 \ln(p_2/p_1)}{T_2 - T_1} \quad (3)$$

where  $p_i$  and  $T_i$  represent the pressure and corresponding temperature of isotherm  $i$ , respectively, and  $R$  is the constant (8.314 J/K·mol). The CO<sub>2</sub> adsorption of PEI(70%)/SiO<sub>2</sub> is a typical chemical adsorption. As shown in Figure 8b, the  $Q_{st}$  of CO<sub>2</sub> adsorption on the adsorbent decreased significantly as the amount of CO<sub>2</sub> adsorption increased. Afterward, the  $Q_{st}$  value was lower than the energy of forming chemical bindings (40 kJ/mol), indicating that it was a physical adsorption process.<sup>22</sup>

Overall, this implies the heterogeneity of the adsorbent surface and obvious advantage for low-pressure CO<sub>2</sub> uptake.

**2.5. Cycle Performance.** To test the regenerative performance of PEI(70%)/SiO<sub>2</sub>, CO<sub>2</sub> adsorption–desorption experiments were carried out, as shown in Figure 9. It can be



**Figure 9.** Cyclic adsorption performance of PEI(70%)/SiO<sub>2</sub> for CO<sub>2</sub> at 25 °C and 1.5 bar.

observed that PEI(70%)/SiO<sub>2</sub> has excellent regeneration capacity, and the CO<sub>2</sub> adsorption capacity has only little fluctuations after 10 subsequent cycles. There was no significant difference in the CO<sub>2</sub> absorption, which means no loss of amine active centers. Therefore, PEI(70%)/SiO<sub>2</sub> is very stable and has outstanding regenerability.

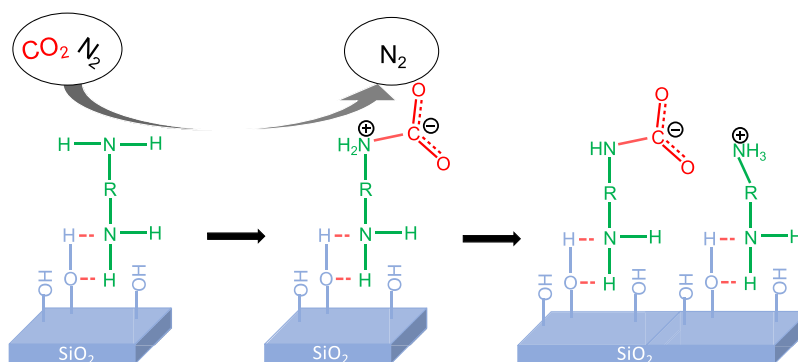
**2.6. Adsorption Mechanism.** Combined with the current experimental results and previous studies,<sup>9,52–54</sup> a plausible carbon dioxide adsorption mechanism is proposed and shown in Figure 10. After immobilization of PEI, SiO<sub>2</sub> adsorbents have more active adsorption sites (e.g., –NH<sub>2</sub>). Thus, CO<sub>2</sub> can be adsorbed chemically to form zwitterions with immobilized amines and, finally, carbamates with higher thermal stability. In addition, CO<sub>2</sub> can also be fixed by hydrogen bonding between silicon hydroxyl and CO<sub>2</sub>. In the adsorption process, abundant alkaline –NH<sub>2</sub> sites are the key reason for the highly selective separation of CO<sub>2</sub> and N<sub>2</sub>.

### 3. CONCLUSIONS

In conclusion, a series of amine-modified amorphous silica was prepared by a simple, green, and efficient mechanical grinding method. The influence of mechanical grinding on amine content, porous structure, and CO<sub>2</sub> adsorption performance was investigated by characterization. The results showed that this method has significant advantages for amine dispersion. The adsorbents also have a remarkably CO<sub>2</sub> adsorption capacity at high temperatures. At 25 °C and 1 bar, its IAST selectivity values for CO<sub>2</sub>/N<sub>2</sub> (15:85) and CO<sub>2</sub>/CH<sub>4</sub> (40:60) were up to 561.0 and 148.0, respectively. The adsorption–desorption tests showed the stability and regeneration of the adsorbent. Therefore, it is proved to be a promising adsorbent for the capture and separation of CO<sub>2</sub> from power-plant flue gas.

### 4. EXPERIMENTAL SECTION

**4.1. Materials.** Polyethyleneimine (PEI,  $M_w = 600$  Da) and silica (SiO<sub>2</sub>, hydrophilic-380 type) were purchased from Energy Chemical Technology Co., Ltd., and Aladdin Biochemical Technology Co., Ltd. China, respectively. All



**Figure 10.** Possible CO<sub>2</sub> adsorption mechanism of the PEI-modified SiO<sub>2</sub> adsorbent.

chemicals were used directly without further purification. CO<sub>2</sub> (>99.99%), N<sub>2</sub> (>99.999%), and CH<sub>4</sub> (>99.999%) were supplied by Guiyang Sanhe Special Gas Center, China.

**4.2. Preparation of Adsorbents by the Ball Milling Method.** The PEI-modified SiO<sub>2</sub> adsorbents were prepared by mechanical ball milling. In a typical synthesis procedure, 0.7 g of PEI was dissolved in 1 mL of methanol and allowed to stir for 30 min. Then, the solution and 1 g of SiO<sub>2</sub> were added to a 45 mL ZrO<sub>2</sub> grinding bowl with 10 ZrO<sub>2</sub> balls (diameter, 10 mm) and ball-milled at 500 rpm for 1 h (forward and reverse rotation for 30 min each) using a vertical planetary mill (YXQM-0.4L, MITR Instrument & Equipment Co., Ltd., China). Finally, the sample was allowed to dry at 80 °C for 12 h. The obtained sample was denoted as PEI(70%)/SiO<sub>2</sub>. Similarly, 30, 50, and 100% PEI-modified SiO<sub>2</sub> adsorbents were synthesized.

**4.3. Preparation of Adsorbents by the Impregnation Method.** The PEI-modified SiO<sub>2</sub> adsorbents were prepared by the impregnation method. In a typical synthesis procedure, a desired amount of PEI was dissolved in 30 mL of methanol. After complete dissolution, 1 g of SiO<sub>2</sub> was added to the solution and stirred for 6 h at 25 °C. Then, the methanol in the mixture was evaporated at 90 °C under vacuum. The sample was dried at 80 °C under vacuum for 12 h. The obtained sample was denoted as IM-PEI(70%)/SiO<sub>2</sub>. Similarly, 30, 50, and 100% PEI-modified SiO<sub>2</sub> adsorbents were synthesized.

**4.4. Characterization of Adsorbents.** FTIR spectra of adsorbents were recorded on a Nicolet iS50 FTIR spectrometer. Thermogravimetric analysis (TGA) was performed using an STA 449F5 simultaneous thermal analyzer over the temperature range of 30 to 500 °C with a heat rate of 10 °C·min<sup>-1</sup> in a N<sub>2</sub> atmosphere. The pore structure of the samples was recorded by a BSD-PS(M) surface area and porosity analyzer (Beishide Instrument-S&T). The surface morphology of adsorbents was determined by scanning electron microscopy (SEM, Hitachi S-3400 N). X-ray diffraction (XRD) was performed on a small-angle X-ray diffractometer (D8 Advance) in the range of 2θ from 5° to 90°.

**4.5. Gas Adsorption Experiment.** CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> adsorption isotherms were determined using the BSD-PS(M) by varying the temperature from 0 °C to 90 °C, and the gas pressure was changed from 0 bar to 1.5 bar. Before the test, the samples were degassed in vacuum at 110 °C for 3 h. The cycle performance was tested by the above process repeating 10 times. Adsorption kinetics was evaluated by a typical procedure, and CO<sub>2</sub> gas (99.99%) was bubbled at a flow rate of about 10 mL·min<sup>-1</sup> through the adsorbent. The CO<sub>2</sub> uptake was measured with an electronic balance.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c04743>.

Details about the structure characterization of the PEI-modified SiO<sub>2</sub> adsorbents and the gas adsorption performance (PDF)

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### Notes

The authors declare no competing financial interest.

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