Role of additives in silica-supported polyethylenimine adsorbents for CO₂ adsorption

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Abstract
SiO₂ aerogels were prepared by sol-gel method and methyl alkylation reaction using TEOS as silicon sources. Silica-supported polyethylenimine (PEI/SiO₂) adsorbents for CO₂ adsorption were prepare by grafting techniques, in which mesoporous SiO₂ aerogel was loaded with PEI and organic compounds functionalized by hydroxyl or amino groups as dopants. CO₂ adsorption isotherms of PEI amine-modified SiO₂ aerogels were measured and the results show that the maximum CO₂ adsorption capacity (1.8 mmol g⁻¹) was obtained over a doped SA-PEI-N-Y loaded with 45% PEI and 15% N-Y (N-[3-(Trimethoxysilyl)propyl]ethylenediamine, denoted as N-Y). In addition, SA-PEI-N-Y has stronger thermal stability than SA-PEI-60% in nitrogen from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. It turns out that N-[3-(Trimethoxysilyl)propyl]ethylenediamine is the best dopant.

1. Introduction

The rapid growth of anthropogenic CO₂ emissions in the atmosphere, especially the CO₂ emissions caused by fossil fuel combustion, has attracted great attention due to the influence of the greenhouse effect [1–3]. On the morning of May 11, 2019, local researchers at the Scripps Institution of Oceanography monitored 415.26 ppm of historical data at the Mona Roa Weather Station in Hawaii, creating the highest ever record. According to the NOAA Earth System Research Laboratory, CO₂ accounts for 63% of all global warming caused by greenhouse gases. Therefore, the development of more efficient carbon dioxide capture and storage (CCS) technology is extremely urgent.

Solid amine-modified adsorbents are mainly composed of supports with highly developed porosity and active components with sites having an affinity for CO₂ [4–7]. For example, Ganesan et al successfully introduced amine functional groups on diatom xerogel (DXEA) silica particles by ring opening mechanism [8]. Amine modified solid adsorbents can be prepared by two techniques. One technique is a wet impregnation method in which liquid amine molecules are impregnated into a porous support via van der Waals forces. Another technique is a grafting process in which an alkanolamine molecule is grafted onto the inner surface of a porous support by reaction with a silanol group [9–12]. The former affords porous support surface-coated with amines, whereas the latter induces the formation of aminosilane-functionalized adsorbents. Most of the amine-based adsorbents reported so far were prepared by wet impregnation with relatively large amine loading. However, amine coated on the support was prone to agglomeration under desorption conditions, which inevitably led to uneven distribution of amines and low utilization efficiency of amine functional groups [13].

Recently, efforts have been made to optimize the amine phase with other additives to obtain adsorbents having higher CO₂ adsorption capacity [14, 15]. In this paper, PEI modified SiO₂ aerogels were grafted with different additives from amine functional groups and hydroxyl groups and emphatically the effects of the seven additives on CO₂ adsorption capacity were investigated and evaluated.

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2. Experimental section

2.1. Materials
Tetraethoxysilane [TEOS, AR; Si(OCH2CH3)4], ammonia solution and deionized water were all obtained from Shanghai Lingfeng Reagent Factory. Trimethyl chlorosilane [TMCS, CP; (CH3)3SiCl], triethylamine [TEA, C6H15N], 2-methylimidazole [2-Ml, 99%; C4H6N2], hydrofluoric acid (HF, AR) and ethanol were purchased from Sinopharm Group Chemical Reagent Co. Ltd. Ethylene glycol [EG, AR; (CH2OH)2], polyethylene glycol [PEG, AR; HO(CH2CH2O)nH] and n-Hexane were produced by Jiangsu Qiangsheng Functional Chemical Co. Ltd. Methyltrimethoxysilane [MTMS, 98%; CH3Si(OCH3)3], hexamethyl disilylamine [HMDS, AR, 98%; C6H19NSi2], phenyltriethoxysilane [PTES, 98%; (CH3CH2O)3SiC6H5], imidazole [Im, 99%; C3H4N2] and polyethylenimine [PEI, Mw = 600, 99%; (CH2CH2NH)n] were provided by Aladdin. N-[3-(Trimethoxysilyl)propyl]ethylenediamine [95%; C8H22N2O3Si] was purchased from Shanghai Macklin Biochemical Co. Ltd. All chemicals were used as purchased without further purification.

2.2. Preparation of SiO2 aerogels
SiO2 aerogels were prepared by sol-gel method and methyl alkylation reaction using TEOS as silica sources. The first step includes the acid-catalyzed hydrolysis of silica sources and the second one is condensation of the silanol groups by the addition of ammonia. A certain volume of anhydrous ethanol, deionized water and TEOS were mixed under stirring for 30 min. Hydrofluoric acid was added dropwise under stirring to provide an acidic environment that is conducive to hydrolysis. 25% ammonia was added to make the mixed solution \( \text{pH} = 7 \sim 8 \) with continuous stirring at room temperature water bath for 1 h. To strengthen the silica network, the aerogels were aged for 3 h at the water bath of 50 °C. Then, the gels were subjected to the pore fluid exchange with ethanol 2 times in 24 h and were washed with n-hexane 3 times in 24 h. Finally, the gels were obtained by drying at 100 °C for 12 h.

2.3. Preparation of PEI amine-modified SiO2 aerogels
PEI and additives were grafted onto a SiO2 aerogel support using conventional grafting techniques. 0.5 g of SiO2 aerogel was added to a conical flask with 30 ml anhydrous ethanol. The solvent was then stirred at room temperature until the suspension was dispersed evenly. The temperature was raised rapidly to 70 °C, and different amounts of PEI and other additives were added dropwise. 1 ml distilled water was added to promote the dispersion and hydrolysis of PEI. The solution was stirred and refluxed continuously for 4 h. The obtained PEI modified SiO2 aerogel was washed repeatedly with ethanol and dried in an oven at 100 °C for 12 h. The synthesis route is shown in figure 1. PEI modified adsorbents were denoted as SA-PEIX-additiveY, with \( X \) representing the weight loadings of PEI on as-prepared adsorbents and \( Y \) denoting the weight percentages of aminosilane or alcohol on SiO2 aerogel supports. In this study, \( X \) was set as 30%, 45% and 60%; \( Y \) was ranged from 0 to 45%. Equations (1) and (2) show the calculation equation of \( X \) and \( Y \).

\[
X = \frac{m_{\text{PEI}}}{m_{\text{PEI}} + m_{\text{SA}}} \times 100\% \quad (1)
\]

\[
Y = \frac{m_{\text{additive}}}{m_{\text{additive}} + m_{\text{PEI}} + m_{\text{SA}}} \times 100\% \quad (2)
\]

where \( m_{\text{PEI}} \) is the weight of added PEI, g; \( m_{\text{additive}} \) is the weight of aminosilane or alcohol, g; \( m_{\text{SA}} \) is the weight of the SiO2 aerogel support, g;

![Figure 1. Synthetic route of PEI/SiO2 adsorbents.](image-url)
2.4. Material characterization

N$_2$ adsorption–desorption isotherms and CO$_2$ adsorption isotherms of SiO$_2$ aerogels were measured by Autosorb-IQ2-2MP-V. Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (TGA/DSC3 + METTLER) in nitrogen from room temperature to 800 °C with the heating rate of 10 °C min$^{-1}$.

3. Results and discussion

3.1. Amine loading of PEI on SiO$_2$ aerogels

According to the definition of the International Union of Pure and Applied Chemistry (IUPAC2015), N$_2$ adsorption–desorption isotherms of SiO$_2$ aerogels modified with PEI at 77 K shown in figure 2 are of type IV, corresponding to characteristic of mesoporous materials. With the increase of PEI-impregnated concentration from 0 to 60 wt%, the nitrogen adsorption capacity of PEI-modified SiO$_2$ aerogels decreased and the hysteresis loops on the isotherm decreased, thus the BET surface area of samples decreased from 823 to 90 m$^2$ g$^{-1}$. It is apparent that PEI penetrated into the pores when SiO$_2$ aerogel was impregnated with 60 wt% PEI, causing pore blockage. Further details on the variation in the BET surface area and pore diameter are described in table 1.

Figure 2(b) is the pore size distribution curves of SiO$_2$ aerogels with the desorption branching curve obtained by the BJH calculation method. Compared with SiO$_2$ aerogel with pore size of about 5 nm, the pore sizes of PEI-modified SiO$_2$ aerogels mainly concentrate on 20 nm, accompanied by a small amount of macropore.

Figure 3 shows the adsorption isotherms and pore size distribution curves of CO$_2$ at 273 K adsorption temperature of SiO$_2$ aerogels modified with PEI. Studies show that as the temperature rises, the amount of
carbon dioxide adsorbed increases first and then decreases [16, 17]. Ganesan Sriram prepared the mesoporous carbon nanospheres (CNSs), which its CO2 adsorption increased and then followed a reduction trend, at the three temperatures [18]. 273 K is the minimum temperature at which carbon dioxide adsorption can be measured. The amine loading increased from 0% to 60% and CO2 adsorption first increased and then decreased. When the amine loading was equal to 45%, the CO2 adsorption capacity was the highest. Compared with SA-PEI-0%, it is found in figure 3(b) that a small amount of micropores, especially SA-PEI-45%, exist in PEI amine modified SiO2 aerogels. On the other hand, when the amine functional groups are loaded on the SiO2 aerogel with high specific surface area, more active sites conducive to CO2 adsorption will be formed, thus CO2 adsorption capacity will increases. On the other hand, with the increase of the amine loading, the inner surface of SiO2 aerogel is occupied by PEI organic amine molecules, resulting in a sharp decrease in the specific surface area of the material. Due to the surface of the adsorbent contains excessive amine functional group molecules, the mass transfer resistance increases when the loading amount of PEI = 60%, which hinders the reaction between CO2 and amine functional groups in the pores. At the same time, the increasing steric hindrance of organic compounds and the reduction of the active site leads to the reaction activity to decrease continuously, and the internal pores are blocked, therefore resulting in a decrease in the CO2 adsorption capacity [19].

3.2. Amine loading of PEI and additives on SiO2 aerogels

There have been several reports that the CO2 adsorption capacity can be significantly elevated by the introduction of some organic compounds functionalized with hydroxyl group or amino group into amine-based sorbents [4, 20]. Therefore, a series of PEI/SiO2 adsorbents were prepared with PEI (30%) and additives (30%) as dopants to improve their adsorption of CO2 under a total loading limitation of 60%. As can be seen from figure 4(a), additives makes the adsorption capacity of SA-PEI-additives to CO2 higher than that of SA-PEI-60%. To a certain extent, additives containing amine or hydroxy functional groups play an important role in promoting the CO2 adsorption capacity of amine adsorbents. Among additives containing amine functional groups, CO2 adsorption capacity of SA-PEI-N-Y reaches a maximum of 1.44 mmol g\(^{-1}\). Moreover, 0.72 and 0.63 mmol g\(^{-1}\) of CO2 are observed over SA-PEI-EG and SA-PEI-PEG with the hydroxyl functional groups of additives, respectively, which are higher than that of SA-PEI-60%. This may imply that some kind of synergistic effect on the CO2 adsorption is possibly derived from the interaction between the amino group and hydroxyl group in the doped PEI/SiO2 adsorbents. Combined with the pore size distribution shown in figure 4(b), we compare SA-PEI-HMDS with SA-PEI-EG and find that not only the surface area of SA-PEI-HMDS is larger than the surface area of SA-PEI-EG but also its the proportion of pore size distribution between 0.3 and 0.6 nm is higher than SA-PEI-EG’s, so SA-PEI-HMDS has a greater CO2 adsorption capacity than SA-PEI-EG. The higher proportion of pore size distribution between 0.3 and 0.6 nm and the larger the specific surface area, the greater the adsorption capacity of CO2. Therefore, PEI/SiO2 adsorbent with the additive of N-[3-(Trimethoxysilyl) propyl]ethylenediamine has the strongest CO2 adsorption capacity.

On account of the highest CO2 adsorption capacity obtained on 30% N-Y + 30% PEI SiO2 aerogels, N-Y can be considered as the best dopant for PEI-modified SiO2 aerogels. Therefore, the CO2 adsorption properties of PEI/SiO2 adsorbents doped with N-Y were further employed under the different mass ratios of PEI and N-Y: (1) In figure 4, the total loading of 60% equal to X% PEI plus Y% N-Y; (2) X and Y ranges from 10 to 45%
respectively. As can be seen from the figure 5, the adsorption capacity of CO₂ on SA-PEI45%-N-Y15% reaches the maximum.

3.3. Adsorption mechanism of CO₂

It is known that carbamates may be formed by a reaction between a primary/secondary amine and CO₂ in the absence of water [21, 22]. One CO₂ molecule consumes two amine functional groups, of which one as a proton receptor and the other as a carbamate anion. The proposed reaction mechanism is as follows:

\[ \text{RNH}_2 + \text{CO}_2 \rightarrow \text{RNH}_2^+ \text{COO}^- \]  
\[ \text{RNH}_2^+ \text{COO}^- + \text{RNH}_2 \rightarrow \text{RNHCOO}^- + \text{RNH}_3^+ \]

where R represents H or alkyl groups. The total reactions are shown below

\[ 2\text{RNH}_2 + \text{CO}_2 \rightarrow \text{RNHCOO}^- + \text{RNH}_3^+ \]
\[ 2\text{R}_1\text{R}_2\text{NH} + \text{CO}_2 \rightarrow \text{R}_1\text{R}_2\text{NCOO}^- + \text{R}_1\text{R}_2\text{NH}_3^+ \]
\[ \text{RNH}_2 + \text{R}_1\text{R}_2\text{NH} + \text{CO}_2 \rightarrow \text{R}_1\text{R}_2\text{NCOO}^- + \text{RNH}_3^+ \]
\[ \text{R}_1\text{R}_2\text{NH} + \text{ROH} + \text{CO}_2 \rightarrow \text{R}_1\text{R}_2\text{NCOO}^- + \text{ROH}_3^+ \]

Taking SA-PEI-HMDS as an example, a CO₂ molecule complex with amine functional groups on PEI and HMDS respectively to form stable ion pairs of carbamate anions and proto-amino cations. For SA-PEI-N-Y, a CO₂ molecule reacts with two amine functional groups on PEI and N-Y, so its CO₂ adsorption capacity (1.44 mmol g⁻¹) is 1.5 times that of SA-PEI-HMDS (0.95 mmol g⁻¹). These mechanisms are based on the accepting protons ability of SA-PEI compounds. Therefore, this mechanism to some extent depends on the...
basicity of these components: amines with higher basicity are more likely to accept protons, thus promoting CO₂ adsorption. Addition of electron group can improve its basicity, while electron-withdrawing group can reduce its basicity. Therefore, for Im and 2-MI, adding electron groups (–CH₃) to Im will lead to a slight increase in CO₂ adsorption capacity. In addition, for SA-PEI-TEA, the basicity of tertiary amines is the weakest on the aliphatic chain. The strength of basicity depends on the combination of the shared electron pair and the proton on the nitrogen atom. Moreover, the ability of nitrogen atoms to accept protons is related to the density of electron clouds on nitrogen atoms and the steric resistance of groups on nitrogen atoms. From the electron-inducing effect, the electron cloud density and basicity of nitrogen atom increase with the increase of the number of alkyl groups on nitrogen atom. Therefore, aliphatic secondary amines are stronger than primary amines, and they are more basic than ammonia. However, from the space effect of alkyl groups, the number of alkyl groups increases, and the space barrier increases correspondingly. The steric effect of the three ethyl groups in triethylamine is more significant than that of electron donation, so the basicity of triethylamine is relatively weak, thus the adsorption capacity of CO₂ decreases.

For the SA-PEI doped with alcohol, some synergistic effect of CO₂ adsorption may be the interaction between the amine functional groups and the hydroxyl group, and the reaction mechanism is shown in equation (6). A CO₂ molecule consumes an amine group on the PEI and a hydroxyl group on the EG or PEG. On the one hand, the addition of hydroxyl group promotes the uniform amine dispersion on the porous silica surface. On the other hand, it plays a synergistic role on the porous silica surface. The larger the molecular weight of alcohol-doped additives, the less effective adsorption sites, resulting in less CO₂ to be absorbed. Therefore, SA-PEI-EG has greater adsorption capacity for CO₂ than SA-PEI-PEG. Molecular diagrams of the adsorption reactions of various combinations of CO₂, amines and alcohols are shown in figure 6.

3.4. Thermal stability of amine-modified SiO₂ aerogels
Thermal stability is one of the most important properties of the practical engineering applicability of adsorbents. Figure 7 demonstrates the thermogravimetric and rate of mass loss of SiO₂ aerogels before and after amine modification. All amine-modified SiO₂ aerogels show their first weight loss peaks from room temperature to 100 °C, which are no more than 8% weight loss attributed to the volatilization of physically adsorbed H₂O, CO₂ and remaining solvent such as ethanol or hexane. The weight loss of SA-PEI-0% is in the range from 145 °C – 800 °C and is about 20% mostly accounted for vaporization of bonding water and the condensation of silanol groups. The TG curves of SA-PEI-30% and SA-PEI-60% show a second weight loss at 160 °C – 500 °C and 235 °C – 450 °C respectively, which are associated with the decomposition of the loaded amine. For SA-PEI-N-Y, SA-PEI-EG, SA-PEI-PEG, SA-PEI-TEA and SA-PEI-HMDS, the beginning decomposition temperatures are 225, 165, 178, 230 and 228 °C, respectively, ranging between SA-PEI-30% and SA-PEI-60%, expect SA-PEI-Im and SA-PEI-2-MI. The formation of hydrogen bonds of amine modified SiO₂ aerogels enhanced the interaction between PEI and support and the initial decomposition temperatures are higher than that of SA-PEI-30%. It is also possible that they are likely due to the formation of chemical bonds between amine functional groups and silica substrate, which require more energy to be destroyed, so they have higher thermal stability. For SA-PEI-Im, SA-PEI-2-MI, SA-PEI-EG and SA-PEI-PEG, the interaction force of amine modified SiO₂ aerogels are small, which may destroy the original stable structure, resulting in poor thermal stability.
4. Conclusions

Silica-supported polyethylenimine (PEI/SiO$_2$) adsorbents for CO$_2$ adsorption were prepared by grafting techniques, in which mesoporous SiO$_2$ aerogel was loaded with PEI and organic compounds functionalized by hydroxyl or amino groups as dopants. The addition of hydroxyl groups or amine functional groups has a certain synergistic effect on CO$_2$ adsorption. As a result, the maximum CO$_2$ adsorption capacity (1.8 mmol g$^{-1}$) was obtained over a doped SA-PEI-N-Y loaded with 45% PEI and 15% N-Y, which has stronger thermal stability.

TOC:
SiO$_2$ aerogels were prepared by sol-gel method and methyl alkylation reaction using TEOS as silicon sources. Polyethylenimine (PEI) and seven additives (amine or hydroxyl functional groups) were grafted onto SiO$_2$ aerogel supports using grafting techniques to increase CO$_2$ adsorption. Moreover, N-[3-(Trimethoxysilyl) propyl]ethylenediamine is the best dopant.

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Conflict of Interest

This manuscript entitled ‘Role of Additives in Silica-Supported polyethylenimine Adsorbents for CO$_2$ Adsorption’ was based on our fundamental research achievements, and the experiment was performed in our own lab which is the key laboratory of Jiangsu Province, P R China. The paper is original and no conflict of interest exists. All authors have read and approved this version of the article, and due care has been taken to ensure the integrity of the work. It is not being submitted to any other journal.

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