Deactivation Kinetics of Polyethylenimine-based Adsorbents Used for the Capture of Low Concentration CO₂

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ABSTRACT: CO₂ emission is generally regarded as the major contributor to global climate change, and polyethylenimine (PEI)-based CO₂ adsorbents are promising materials for the capture of low concentration CO₂. This paper deals with the deactivation kinetics of PEI-based CO₂ adsorbents used for the capture of low concentration CO₂. EA and TG analyses demonstrated that thermal degradation and O₂-induced deactivation of the adsorbents occurred simultaneously under air exposure conditions. It was found by N₂ exposure experiments at the temperature of 50–80 °C that the thermal degradation of PEI-based adsorbents followed a first-order reaction model with an activation energy of 80.98 kJ/mol and a pre-exponential factor of 6.055 × 10⁶ (h⁻¹). The parallel reaction model was employed to distinguish the O₂-induced deactivation from the thermal degradation of the adsorbents through air exposure experiments within 50–80 °C. The O₂-induced deactivation exhibited a second-order reaction with an activation energy of 74.47 kJ/mol and a pre-exponential factor of 6.321 × 10⁶ (% × h⁻¹). The results of simulating the overall deactivation of the adsorbents by the parallel reaction kinetic model were well consistent with those of the experiments, proving that the parallel reaction model was feasible for the description of the deactivation of PEI-based adsorbents.

1. INTRODUCTION

CO₂ emission is generally regarded as the major contributor to global climate change. Different approaches exploited for capturing or separating CO₂ include absorption into liquid solvents,† permeation through membranes,† and adsorption on solids as well. Liquid absorption is efficient for CO₂ removal, but most often requires high regeneration energy. The membrane separation process faces the challenge of the long regeneration rate. The technology of adsorption has drawn particular attention because of its high efficiency and lower energy consumption. The interest in the use of amine-based adsorbents inspired by liquid amine solvent technology has increased during the last few years.‡ Amine-based adsorbents capture CO₂ by the chemical mechanism with the virtues of high adsorption efficiency, easy regeneration, and tolerance to water. Polymeric amine-based adsorbents, such as polyethylenimine (PEI), are achieving higher thermal stabilities and a better adsorptive effect of CO₂ compared to small molecule amine adsorbents.²⁰

Stability or service life of the CO₂ absorbent is a key index in the evaluation criterion of adsorbent properties.¹¹ Physical conditions including adsorption/desorption time, temperature, and pressure affect the stability of the adsorbents. Moreover, chemical factors, especially the interactions between amine and H₂O,¹² SO₂,¹³ H₂S,¹⁴ NO,¹⁵ O₂,¹⁶ and CO₂¹⁷ deactivate the amine-based adsorbents. In the capture of low concentration CO₂ such as direct air capture (DAC) of CO₂ from ambient air or closed cabins, H₂O, O₂, and CO₂ are the likely ingredients that deactivate adsorbents. The service life of CO₂ amine-based adsorbents is mainly determined by the stability of amines, which could be concluded to four major factors:¹⁸ effective component loss subjected to physical effect, thermal degradation, CO₂-induced deactivation, and O₂-induced deactivation. Drage et al.¹⁹ observed a great loss in CO₂ adsorption capacity with concentrated CO₂ as the regeneration purge gas at desorption temperatures of 110–140 °C, which attributed to the chemical reaction of CO₂ with amines on PEI and the irreversible formation of urea at elevated temperatures. Didas et al.²⁰ evaluated the thermal instability of materials with methyl amine functionality through the loss of organic content at elevated temperatures. Calleja et al.²¹ found that nitrogen content decreased to a small extent for amine-functionalized SBA-15 materials dried in air atmosphere at 110 °C, while the materials showed a significant decrease in CO₂ adsorption capacity. Cedelonio et al.²² validated the lower stability of amine-based adsorbents under CO₂/air than CO₂/N₂ conditions, indicating that O₂ accelerated the deactivation of the amine adsorbent. Different groups²²–²³ have reported that primary and tertiary monoamines kept stable during the long term adsorption/desorption cycles at different temperatures while secondary monoamine was more liable to oxidative degradation, and mixed amines were most sensitive. Based on the dominant reactions between O₂ and monoethanolamine (MEA), Percy et al.²⁴ constructed a dynamic mathematical

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model from the first principles for the CO$_2$ absorber column to quantify the loss of MEA through oxidative degradation, demonstrating that the concentrations of CO$_2$, O$_2$, and H$_2$O affect the degradation rate of MEA. Svendsen et al. conducted the experimental studies on the oxidative degradation of MEA and concluded that the temperature had a higher impact on MEA loss than oxygen concentration. Deactivation kinetics of amine has been studied in depth in association with CO$_2$ absorption in amine solutions and the thermal stability of PEI-based CO$_2$ adsorbents had been explored at elevated temperatures between 110 and 180 °C. However, few studies were reported on the deactivation kinetics of solid amine adsorbents upon long term exposure to air, especially for the adsorbent used in the DAC process that characterized with low CO$_2$ concentration and temperature. CO$_2$ may take part in the deactivation under high temperature and CO$_2$ concentration, such as 100 °C with pure CO$_2$. Considering the low concentration of CO$_2$, it is reasonable to ignore the effect of CO$_2$ on the degradation of PEI-based adsorbents in this research. On the opposite, the effect of O$_2$ on the degradation of amine-based adsorbents is much greater because the concentration of oxygen is 50−500 times that of carbon dioxide. Though the ignorance of the effect of CO$_2$ simplified the issue, a major problem rose from the existence of a large amount of O$_2$, which is the co-existence of thermal degradation and O$_2$-induced deactivation in the system. Another problem was that the deactivation of the amine-based adsorbent operated under mild conditions is a long term time-dependent change. It had reported that little change in the properties of the PEI-based CO$_2$ adsorbent had been observed after 2000 absorption/desorption cycles under 20−30 °C. Surely, it would be time and energy consuming if the study was conducted at the working temperatures of the PEI-based adsorbent. The work was an attempt to establish the kinetic model for the deactivation of PEI-based absorbents used at ambient temperature. A parallel reaction model was employed in the work to resolve the thermal and O$_2$-induced deactivations that occurred simultaneously. The deactivation kinetics of the PEI-based adsorbent was then explored within a suitable range of temperature so that the kinetic model could be extrapolated, in a more practical and feasible way, to the temperature at which the PEI-based adsorbent is operated.

The deactivation kinetic of the PEI-based CO$_2$ adsorbent plays a significant role in determining the reaction mechanism, estimating the influences of different operation conditions, and providing effective methods to prevent the rapid deactivation of the adsorbents. Accurate kinetic models could be applied to evaluate adsorbent performance and support the designs of reactors and processes. The model of the deactivation kinetics established at reasonable temperatures is also an approach for the prediction of the service life of the PEI-based adsorbent used at 20−30 °C.

2. RESULTS AND DISCUSSION

2.1. Experimental Temperature. TGA (TA Instruments, SDT Q600) was employed to investigate the effect of temperature on the stability of the PEI-based adsorbents. The weight loss curves of the adsorbents and support, the porous polymer resin are presented in Figure 1a and their derivatives, in Figure 1b.

It could be seen from Figure 1 that the mass loss of adsorbents started to decrease around 200 °C, meaning the temperature of the deactivation study should not be higher than 200 °C. Almost no signs of weight loss are observed for both the support and PEI-based adsorbent below the temperature of 100 °C, indicating the deactivation study can be conducted below 100 °C in principle. However, the deactivation mechanism of the PEI-based adsorbent may vary with temperatures. To reduce as much as possible the likely bias caused by deviating from the true deactivation mechanism, the experiment for kinetic studies was conducted below 80 °C with the lowest temperature at 50 °C to make sure of a reasonable deactivation speed.

2.2. O$_2$-Induced Deactivation Reaction. On the setup of Figure 2, the deactivations of PEI-based adsorbents were performed under different temperatures. The amino group losses measured by the weighing method are presented in Figure 2.

It shows from Figure 2 that the mass loss of adsorbents increases with exposure time both in N$_2$ and simulated air atmospheres. Meaningfully, the mass loss of adsorbents in N$_2$ is generally greater than that in simulated air at all the three temperatures.

It has been reported that the weight change after oxidation treatment did not appear to track the stability of the adsorbents for carbon capture applications. The reason is mainly due to the co-existence of thermal degradation and O$_2$-induced deactivation, and the latter is connected with oxygen addition and weight gain. It is, thus, reasonable to speculate that some oxygen addition reaction occurs when the PEI-based adsorbent is exposed to simulated air. The speculation is supported by the literature observations of the formation of urea and organic acids linkages at the expense of amino groups.
Evidence of the oxygen addition reaction is also given by elemental analysis (Elementar, Vario MICRO). The results of the elemental analysis of PEI extracted from the adsorbents are presented in Table 1. It shows that 67 °C N₂ exposure process results in higher contents of C, H, and N than air exposure, and lower air exposure temperature, 67 °C, results in higher contents of C, H, and N than higher temperature (80 °C). Because few other elements except N, H, and C are introduced into the system in the air exposure process, the declining of the contents of C, H, and N in the adsorbent should be contributed by the O-addition reaction.

The results above support that O-addition reaction occurs with thermal degradation when the adsorbent is exposed to simulated air. It needs finding a way to distinguish the two reactions from each other to establish a proper kinetic model of deactivation.

2.3. Data Collection. The weighing method determines the amino group content for the process of single decomposition of the PEI-based adsorbent, but is not applicable for the process of air exposure deactivation because of the presence of O-addition, which increases the weight of adsorbents by binding oxygen atoms. On the other hand, CO₂-adsorption method works for both N₂ and air exposure processes as it "titrates" amino groups directly. However, the weighing method is not only convenient, but also has better reproducibility than the CO₂-adsorption method, as long as the weighing method is applicable. Figure 3 presents the comparison of the results of the two methods, showing that experimental datum points by the weighing method result in even curves while those by the CO₂-adsorption method are uneven. Thus, the weighing method is favored whenever it is applicable in the study.

Although the weighing method is favored, some error of the weighing method should not be ignored. Figure 3 shows that the in N₂-exposure process, the difference between the PEI losses measured by the two methods is not very significant before 1000 h, but after 1000 h the bias increases gradually with time. The systematic error of the weighing method is introduced from the existence of a small amount of O₂ in the reaction system, which leads to significant O-addition when the reaction time is long enough. For the air exposure process, the CO₂-adsorption method is obviously more reliable because of the existence of O-addition. Therefore, the data for kinetic studies are collected on the setup of Figure 8 with both weighing and CO₂-adsorption methods. By applying the data to parallel-reaction mode, the thermal degradation, and O₂-induced deactivation processes are thus able to be distinguished satisfactorily for the air exposure deactivation of the PEI-based adsorbent.

2.4. Kinetics of Thermal Degradation. The deactivation of the adsorbent under a nitrogen atmosphere is mainly thermal degradation and thus O₂-induced deactivation is ignored because little oxygen exists in the reaction system. In this case, the weight loss of adsorbents is contributed by PEI thermal degradation and the degradation rate is determined with the data obtained by the weighing method.

The foundation for the study of kinetic data from the PEI loss curve is based on the basic rate equation

\[ r = \frac{\text{d}c_A}{\text{d}t} = kf(c_A) \]

where \( k \) is the rate constant,

\[ f(c_A) = c_A^n \]

\( n \) is reaction order.

Substituting \( n = 0, 1, \) and \( 2 \) into eqs 1 and 2 gives

\[ c_{A_0} - c_A = k_d + e \quad n = 0 \]

\[ \ln \frac{c_{A_0}}{c_A} = k_d + f \quad n = 1 \]

\[ \frac{1}{c_A} - \frac{1}{c_{A_0}} = k_d + g \quad n = 2 \]

where \( t \) represents reaction time, \( e, f, \) and \( g \) are constants.

The N₂ exposure experiments of the adsorbent at 67 and 74 °C are performed and the deactivation curves are presented in Figure 4.

Table 1. Results of Elemental Analysis of PEI before and after Deactivation

| temperature (°C) | exposure gas | exposure time (h) | C (%) | H (%) | N (%) | O calculated (%) |
|-----------------|--------------|-------------------|-------|-------|-------|-----------------|
| no exposure (fresh adsorbent) | | | 55.31 | 9.20 | 27.80 | 7.69 |
| 67 | N₂ | 636 | 54.30 | 9.04 | 26.03 | 10.63 |
| 67 | simulated air | 636 | 53.88 | 8.96 | 25.25 | 11.91 |
| 80 | simulated air | 550 | 53.18 | 8.58 | 23.38 | 14.86 |

Figure 2. Curves of adsorbent mass losses measured by the weighing method at different temperatures.

Figure 3. Amino group losses measured by weighing and CO₂-adsorption methods.
The values of thermal degradation rate constant $k_D$ under 67 and 74 °C for $n = 0$, 1, and 2 are listed in Table 2. Judged by the values of $R^2$, the coefficient of correlation, the thermal degradation of the adsorbent is most likely of first-order ($n = 1$), namely

$$\ln \frac{C}{C_0} = k_D t + f$$ \tag{4}

$$\ln \frac{C}{C_0} = k_D t + f$$ \tag{5}

Table 2. Kinetic Characters of Thermal Degradation for Different Reaction Orders

| reaction order | 67 °C | $R^2$ | 74 °C | $R^2$ |
|----------------|-------|-------|-------|-------|
| 0              | 0.00424 (%·h⁻¹) | 0.98033 | 0.0052 (%·h⁻¹) | 0.94085 |
| 1              | $2.23 \times 10^{-3}$ (%·h⁻¹) | 0.99488 | $3.94 \times 10^{-4}$ (%·h⁻¹) | 0.97869 |
| 2              | $2.49 \times 10^{-3}$ (%·h⁻¹) | 0.98557 | $3.42 \times 10^{-5}$ (%·h⁻¹) | 0.95700 |

Substituting the thermal degradation rate constants of 67 and 74 °C into the Arrhenius equation

$$k = A \exp \left(-\frac{E_A}{RT}\right)$$ \tag{6}

where $A$ is a pre-exponential factor, $E_A$ is activation energy, $R$ is the universal gas constant (8.314 J/mol K), and $T$ is the temperature in K. The activation energy ($E_A$) and the pre-exponential factor ($A$) of thermal degradation are 79.76 kJ/mol and $3.957 \times 10^4$ (h⁻¹), respectively. Thus, the relationship between reaction temperatures and thermal degradation rate constants, $k_D$, is

$$\ln k_D = -\frac{9594}{T} + 19.80$$ \tag{7}

An experiment of N₂ exposure of the PEI-based adsorbent was conducted at 50 °C for the validation of the first-order kinetic model. The curve of the thermal degradation via the weighing method is shown in Figure 5. By eq 5, the rate constant of the thermal degradation at 50 °C is calculated as $k_{D50°C} = 2.516 \times 10^{-3}$ (h⁻¹) from the slope ($R^2 = 0.9959$). Compared with $k_{D50°C} = 5.038 \times 10^{-3}$ (h⁻¹) calculated by eq 7, the relative error is about 2%. The simulation curve modeled by the 50 °C thermal degradation with eq 5 is also shown in Figure 5. It can be seen that the first-order kinetic model agreed with experimental data.

![Figure 4. Deactivation curves of N₂ exposure experiments.](image)

![Figure 5. The comparison of 50 °C thermal degradation and simulation with the first-order kinetic model.](image)

To improve the model’s reliability, the experiment of 50 °C thermal degradation was introduced to determine the reaction active energy. With $k_{D50°C}$, $k_{D74°C}$, and $k_{D74°C}$, the activation energy and the pre-exponential factor of the thermal degradation are modified to 80.98 kJ/mol and $6.055 \times 10^8$ (h⁻¹), respectively, on the basis of Arrhenius eq 6. The relationship between reaction temperatures and thermal degradation rate constants is calibrated as

$$\ln k_D = -\frac{9740}{T} + 20.22157$$ \tag{8}

2.5. Kinetics of O₂-Induced Deactivation. The deactivation data of the adsorbent exposed to simulated air was obtained by the CO₂-adsorption method. As thermal degradation and O₂-induced deactivation occurred simultaneously in the air exposure process of the PEI-based adsorbent, the reaction was then considered a parallel reaction shown as the following

$$k_{D} \quad \text{thermal degradation product}$$

$$k_{O} \quad \text{O₂-induced deactivation product}$$

$k_{D}$ of different temperatures could be resolved by eq 8, while $k_{O}$ as well as the reaction order of O₂-induced deactivation are to be determined. According to the general scheme for amine oxidation

$$\text{Amine} + \text{O}_2 \rightarrow \text{oxidized product}$$ \tag{9}

the oxidation rate at a particular temperature could be represented as

$$r_O = k_{O}P_{O_2}m \cdot C_A^n$$ \tag{10}

where $k_{O}$ is the rate constant of O₂-induced deactivation, $P_{O_2}$ is instantaneous O₂ partial pressure during adsorption, $m$ and $n$ are orders of reaction with respect to O₂ and amine, respectively.

There being little change in the air exposure process, $P_{O_2}$ is taken as a constant and $k_{O}P_{O_2}m$ is lumped into the rate constant, $k_{O}'$, leading to

$$r_O = k_{O}'C_A^n$$ \tag{11}

The total rate of the loss of amino groups in the parallel reaction is the sum of thermal degradation and O₂-induced deactivation rates

$$r_A = r_D + r_O$$ \tag{12}
Substitute eqs 4 and 11 into eq 12 gives
\[
\frac{d\Delta \alpha}{dt} = \frac{d\Delta m_1}{dt} + \frac{d\Delta m_2}{dt} = k_{D}\alpha + k_{O}\alpha^n
\] (13)
Substituting the reaction orders \((n = 0, 1, 2)\) of O-degradation into eq 13 and integrating gives
\[
k_O + k_D\alpha = e^{-k_d t} + p, \quad n = 0
\] (14-1)
\[
\ln \frac{\alpha}{\alpha_0} = (k_D + k_O)t + q, \quad n = 1
\] (14-2)
\[
e^{k_d t} = \frac{u_D}{k_D\alpha} + u, \quad n = 2
\] (14-3)
where \(p, q, u\), and \(u\) are constants.

The air exposure experiments of the adsorbent at 60, 67, and 74 °C are performed and the deactivation curves are presented in Figure 6.

![Figure 6. Deactivation curves of amine-based adsorbent under air exposure.](image)

The deactivation curves fitted with eqs 14-1-14-2-14-3, and the resulting parameters are reported in Table 3. It is found that the fitting of the second-order reaction, \(n = 2\), is the best in general by the values of \(R^2\). Thus, O2-induced deactivation rate, \(r_O\), and the content of the amino group in the adsorbent, \(c_A\), are expressed as
\[
r_O = k_{O}\alpha^n
\] (15)
\[
e^{k_d t} = \frac{1}{k_D\alpha} + \frac{1}{w}
\] (16)
where \(w\) is constant.

Using the values of \(k_O\) of 60, 67, and 74 °C reported in Table 3, the activation energy (72.99 kJ/mol) and the pre-exponential factor \([3.751 \times 10^6 \text{(%-1-h}^{-1})]\) of the pseudo-second-order oxidative degradation are obtained based on Arrhenius eq 6. The relationship between reaction temperature \(T\) and rate constant \(k_O\) is then expressed as
\[
\ln k_O = -\frac{8779}{T} + 15.14
\] (17)

An experiment of air exposure of the PEI-based adsorbent was conducted at 50 °C for the validation of the parallel reaction model. The curve of the air exposure process obtained by the CO2-adsorption method is shown in Figure 7.

![Figure 7. The results of 50 °C air exposure of the adsorbent and the predictions by the parallel reaction model.](image)

Substituting \(k_D\) (50 °C) calculated by eq 5 into eq 16 and plotting e\(^{k_d t}\) with \(k_D/c_A\), \(k_O\) (50 °C), the rate constant of O2-induced deactivation at 50 °C, is obtained as 5.733 \(\times 10^{-6}\) (%\(^{-1}\)-h\(^{-1}\)) with a \(R^2\) of 0.9855 from the slope and intercept of the generated line. Compared with \(k_O\) (50 °C) = 5.960 \(\times 10^{-6}\) (%\(^{-1}\)-h\(^{-1}\)) calculated by eq 15, the relative error is about 4%.

The simulation curve modeled by the 50 °C O2-induced deactivation with eq 16 is also shown in Figure 7. It can be seen from Figure 7 that the parallel reaction model consists of first-order thermal degradation and second-order O2-induced deactivation agrees well with the experimental data. The average of absolute relative deviation of the simulation is 2.7% calculated by
\[
\text{AARD, %} = \frac{100}{n} \sum_{i=1}^{n} \frac{|\hat{y}_i - y_i|}{y_i}
\] (18)

where \(\hat{y}_i\) and \(y_i\) are the predictive and experimental value, \(n\) is the number of data points, and \(i\) represents the \(i\)-th data point.

The validation confirmed that the parallel reaction model is reliable in the description of the overall O2-induced deactivation of the PEI-based adsorbent.

To make the parallel reaction model more reliable, the rate constant of O2-induced deactivation \(k_O\) (50 °C) = 5.733 \(\times 10^{-6}\) (%\(^{-1}\)-h\(^{-1}\)) is introduced to determine the active energy. With \(k_O\) (50 °C), \(k_O\) (60 °C), \(k_O\) (67 °C), and \(k_O\) (74 °C), the activation energy and the pre-exponential factor of O2-induced deactivation are modified to 74.47 kJ/mol and 6.321 \(\times 10^6\) (%\(^{-1}\)-h\(^{-1}\)), respectively, on the basis of the Arrhenius equation. The relationship between reaction temperatures and the rate constant of O2-induced deactivation then becomes

### Table 3. Kinetic Characters of O2-Induced Deactivation for Different Reaction Orders

| reaction order | 60 °C | 67 °C | 74 °C |
|----------------|------|------|------|
|                | \(k_O\) | \(R^2\) | \(k_O\) | \(R^2\) | \(k_O\) | \(R^2\) |
| 0              | 0.00151 (%\(^{-1}\)-h\(^{-1}\)) | 0.9570 | 0.00356 (%\(^{-1}\)-h\(^{-1}\)) | 0.9764 | 0.00447 (%\(^{-1}\)-h\(^{-1}\)) | 0.9427 |
| 1              | 1.28 \(\times 10^{-4}\) (h\(^{-1}\)) | 0.8602 | 3.30 \(\times 10^{-4}\) (h\(^{-1}\)) | 0.8902 | 4.20 \(\times 10^{-4}\) (h\(^{-1}\)) | 0.9729 |
| 2              | 1.26 \(\times 10^{-4}\) (%\(^{-1}\)-h\(^{-1}\)) | 0.9388 | 2.66 \(\times 10^{-4}\) (%\(^{-1}\)-h\(^{-1}\)) | 0.9876 | 3.63 \(\times 10^{-5}\) (%\(^{-1}\)-h\(^{-1}\)) | 0.9719 |
$\ln k'_O = -\frac{8958}{T} + 15.66 \tag{19}$

3. CONCLUSIONS
Studies of the N$_2$ exposure of the adsorbent within 50–80 °C illustrated the thermal degradation of the PEI-based CO$_2$ adsorbent, followed by a first-order reaction model with an activation energy of 80.98 kJ/mol and pre-exponential factor of $6.055 \times 10^8$ (h$^{-1}$). Under air exposure condition, O$_2$-induced deactivation and thermal degradation of the adsorbent occurred simultaneously. Employing a parallel reaction model into the reaction system, the O$_2$-induced deactivation was distinguished from the thermal degradation, and the O$_2$-induced deactivation reaction of the adsorbent exhibited a second-order reaction with an activation energy of 74.47 kJ/mol and pre-exponential factor of $6.321 \times 10^6$ (%$^{-1}$·h$^{-1}$). The parallel-reaction kinetic model established at elevated temperatures successfully predicted the overall deactivation of the PEI-based adsorbent performed at 50 °C, proving it was a feasible model to describe the deactivation of the adsorbent.

4. MATERIALS AND METHODS

4.1. Preparation of the Adsorbent. Branched PEI (M$_w$ = 600, Shanghai Aladdin Bio-Chem Technology Co., Ltd, China) dissolved in methanol (Sinopharm Chemical Reagent Co., Ltd, China) solution was impregnation liquor for porous polyacrylamide microspheres (Knowledge & Benefit Sphere Tech. Co., Ltd, China). Considering the CO$_2$ uptake and the stability, ~15 wt % PEI-loaded adsorbents were obtained by evaporating the solvents. The surface areas and pore structures of the adsorbents were determined with a Quantachrome Autosorb-IQ2-MP apparatus and the particle size distribution was evaluated on an LS-230 Coulter Laser Granularity analyzer. The physical parameters of the adsorbent were listed in Table 4.

4.2. Experimental Procedure. The deactivation of PEI-based adsorbents was tested on the setup, as shown in Figure 8. The setup consists of mass flow controllers (D08-2F, Sevenstar Electronics Co., Ltd, China), thermostat (AT-950, Automatic Science Instrument Co., Ltd., China), IR gas analyzer (GXH-510, Xibi Instrument Co. Ltd., China), and Φ16 × 100 mm stainless-steel tube reactors (self-made) packed with ~7 g of PEI-based adsorbent. Adsorbents were pretreated in the reactor under 50 °C with 500 mL/min of nitrogen gas (99.99%, Hangzhou Jingong Specialty Gases Co., Ltd, China) for 24 h to remove small molecular components like H$_2$O and CO$_2$. The thermostat was then set to the required temperatures under either simulated air (79% N$_2$ + 21% O$_2$, Hangzhou Jingong Specialty Gases Co., Ltd, China) or N$_2$ for deactivation experiments.

4.3. Methods for the Determination of the Amino Group. The amount of the remaining amino group of PEI on the adsorbent was determined with weighing and CO$_2$-adsorption methods. The weighing method measured the loss of adsorbents and obtained the weight loss curve of the adsorbent over time. Because the polymer support is thermostable below its decomposition temperature, the weight loss of the adsorbent was contributed by the deactivation of amino groups. The CO$_2$-adsorption method measured the change of the CO$_2$ adsorption capacities before and after the deactivation was performed on the setup, as shown in Figure 9.

The setup consisted of mass flow controllers (D08-2F, Sevenstar Electronics Co., Ltd, China), thermostat (AT-950, Automatic Science Instrument Co., Ltd., China), IR gas analyzer (GXH-510, Xibi Instrument Co. Ltd., China), and Φ16 × 100 mm stainless-steel tube reactor (self-made). In the system, the CO$_2$ concentration of the outlet of the tube reactor was monitored by an IR gas analyzer. The presence of amino groups on the adsorbent clearly determined the content of CO$_2$ adsorption$^{-1}$ and the loss of CO$_2$ adsorption capacity was primarily due to the degradation of amino groups. The amino groups of PEI-based adsorbents, therefore, were determined by the CO$_2$-adsorption method according to the following reaction:

$$\text{PEI} + \text{CO}_2 \rightarrow \text{CO}_2 \text{PEI}_2$$

The CO$_2$ adsorption capacity $q_a$ (mmol CO$_2$/g adsorbent) on the adsorbent over the adsorption time is calculated by integrating the corresponding breakthrough curves.
where \( T_0 = 273 \text{ K} \), \( T \) is the adsorption temperature in K, \( t_s \) is the adsorption time in min, \( Q_s \) is the volumetric flow rate of the gas in mL/min, \( c_a \) and \( c_{a,\text{out}} \) are the CO\(_2\) concentrations of the inlet and outlet gas flows in vol \%, \( m_i \) is the mass of the adsorbent in the tube reactor in g, and \( V_{m,i} = 22.4 \text{ L/mol} \).

CO\(_2\) uptake is mainly contributed by the amino groups of the adsorbent, and the maximum CO\(_2\)/N ratio achievable by the chemical reaction with solid amine adsorbents is 0.5 mol of CO\(_2\)/mol of N as eq 1. So the amino group content, \( c_A \) (wt \%), was calculated by

\[
c_A = c_{A,0} - \Delta m = q_a \times \frac{2M_{\text{PEI}}}{1000} \approx \frac{q_a \times 43}{500}
\]

where \( c_{A,0} \) is the content of amino groups after pretreatment in wt \%, \( \Delta m \) is the weight loss of amino groups in wt \%, and \( M_{\text{PEI}} \) is the molecular mass of PEI chain unit in g/mol.

The initial CO\(_2\) uptake of the adsorbent for 0.4\% (v) CO\(_2\) at 20 \({}^\circ\text{C}\) is about 50 mg/g.

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