

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263958096>

CO₂ Desorption Kinetics for Immobilized Polyethylenimine (PEI)

ARTICLE *in* ENERGY & FUELS · DECEMBER 2013

Impact Factor: 2.79 · DOI: 10.1021/ef401879z

CITATIONS

4

READS

34

3 AUTHORS, INCLUDING:



Larry Shadle

National Energy Technology Laboratory

85 PUBLICATIONS 485 CITATIONS

SEE PROFILE

CO₂ Desorption Kinetics for Immobilized Polyethylenimine (PEI)

Esmail R. Monazam,^{†,‡} James Spenik,^{†,‡} and Lawrence J. Shadle^{*,†}

[†]National Energy Technology Laboratory, U.S. Department of Energy, 3610 Collins Ferry Road, Morgantown, West Virginia 26507-0880, United States

[‡]REM Engineering Services, PLLC, 3537 Collins Ferry Road, Morgantown, West Virginia 26505, United States

ABSTRACT: The CO₂ desorption rate from CO₂-loaded immobilized polyethylenimine (PEI) on mesoporous silica was investigated in a fluidized bed unit. Nonisothermal studies were carried in the temperature range of 340–380 K and different heating rate (1.0–2.7 K/min). The tests were performed using two different inlet CO₂ concentrations, mainly 16.5% and 33%. The kinetics involved in CO₂ desorption was studied by applying various analytical techniques (model-free and model-fitting) to the nonisothermal data. The model-free approach represented by the nonisothermal isoconversional methods revealed that the apparent Arrhenius parameters (A and E_a) increased with extent of conversion for $0 \leq X \leq 0.3$, followed by an approximately nearly constant value at the higher CO₂ desorption levels. In the constant- E_a region, the nonisothermal CO₂ desorption follows a two-dimensional diffusion model. The apparent Arrhenius parameters ($\ln A$ and E_a) evaluated were 71.3 ± 3.6 and 230.5 ± 13.0 kJ/mol, respectively.

1. INTRODUCTION

Carbon dioxide (CO₂) is an omnipresent species in the flue gas of fossil fuel combustion that has become critically scrutinized with respect to its potential impact on global climate change. Absorption of CO₂ with amine-based solvents is considered to be the most promising choice for CO₂ separation from flue gas. Although several commercial technologies that utilize amine-based solvents are offered in gas processing, the cost of CO₂ capture is still too high and is the major barrier for the wide application of CO₂ capture in power plant sector.^{1,2} This has resulted in a global research effort to mitigate the emissions of CO₂ and examine ways to capture CO₂ directly from power plant flue gases.³

In the past decade, various solid amine sorbents have been investigated worldwide for CO₂ capture.^{4–14} Adsorption of gases onto solid adsorbents has great environmental significance since it can effectively remove pollutants from gaseous streams. Pressure swing adsorption and regeneration is not suitable for retrofit applications such as on existing power plants because of the projected costs of flue gas compression or evacuation. Thermal swing processes are favored for these applications. The amine-based solid sorbent has the potential to reduce the energy requirement for CO₂ desorption by regenerating at relatively low temperatures (e.g., 343 K). The energy for the thermal swing regeneration can be obtained from low-grade heat or waste heat rather than the high-grade steam from the steam cycle.¹⁵ There are very few relevant kinetic studies on the CO₂ release rates for thermal swing processes using this type of amine-based sorbent. As the low-temperature regeneration results in low reaction kinetics, technologies such as vacuum or inert gas sweeping have been widely used to improve the CO₂ desorption kinetics by increasing the driving force of the mass transfer.¹⁶

In this study, we conducted a subsequent study on desorption features of immobilized polyethylenimine (PEI) on mesoporous silica which were used in our previous studies.¹⁷ Amine-based solid sorbent are evaluated by comparing the

desorption rate data obtained under nonisothermal conditions to a wide range of reaction models. To our knowledge, the results on both desorption kinetics and nonisotherms as well as correlations of the model-fitted parameters has never previously been reported, and this study leads to a deeper understanding of the intrinsic reaction mechanisms.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation and Characterization. Sorbent AX was manufactured by Pressure Chemicals polyethylenimine (PEI) on a silica substrate (PQ Inc. 2129).⁴ The particle density was 0.88 g/cm³, and the Sauter mean particle size was 115 μm (Figure 1). The material was sieved by PSRI Inc. removing all of the fines which passed a 125 US mesh screen.

The CO₂ is adsorbed onto PEI, a polymer of 1,2-ethanediamine and aziridine. The PEI used in this sorbent had a number average molecular weight of 2000. The resulting polymer contained a mixture of primary, secondary and tertiary amines. The PEI in BASF's Lupasol PR8515 was approximately 25, 50, and 25% wt primary, secondary, and tertiary amine, respectively. In general, the stoichiometry of CO₂ uptake is 2:1 for primary and secondary amines but is more complex with tertiary amines. In the presence of water the tertiary amine reacts with CO₂ to produce a tertiary ammonium bicarbonate, but in dry environment the tertiary amine reacts in combination with both CO₂ and a primary or secondary amine in a two step process to form the carbamate product. TGA testing in a dry environment indicated that the reaction order for CO₂ on PEI was 0.69; this compares favorably with the theoretical value of 0.625.⁴ The nature of the amine functional groups determines the energy required for regenerating the sorbent.⁷

To prepare the PEI loaded sorbent the PEI was dissolved into water and mixed with the silica substrate in the weight ratio amine:methanol:silica of 0.40:2.0:1.0, respectively. This mixture was then dried using a rotary evaporator. In this fashion, PEI (nominally 40% by weight) was immobilized onto the substrate. This impregnation procedure was reported to produce a well-distributed layer of PEI on mesoporous silica substrate.⁴ Xu et al. reported that there was a

Received: September 18, 2013

Revised: November 22, 2013

Published: November 29, 2013



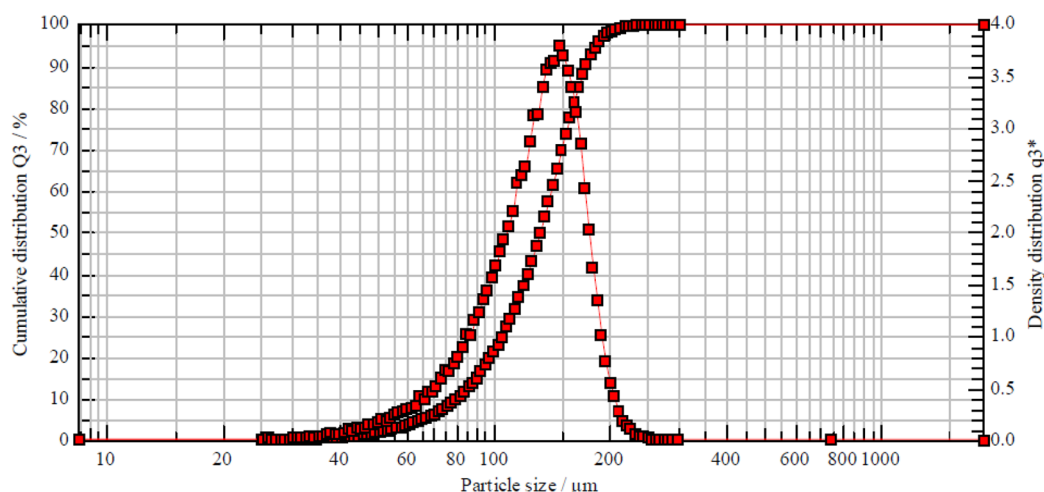


Figure 1. Particle size distribution for sorbent AX.

synergistic increase in adsorption capacity when using the mesoporous substrate over that observed on PEI.¹⁸ This “molecular basket” increases the capacity when PEI loadings exceed 20% by weight. The maximum synergistic effect was found for 50% PEI mixture with mesoporous silica.

2.2. Experimental Apparatus and Procedure. The fluidized bed vessel used was a vertically mounted, 16.5 OD, 13.6 cm ID, 101 cm long high density polyethylene pipe (Figure 2). A 7.5 cm longer

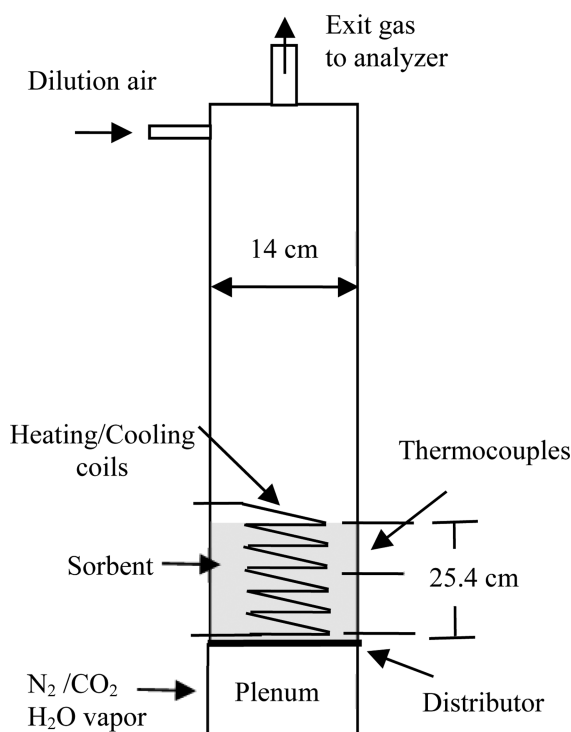


Figure 2. Schematic diagram of experimental apparatus.

plenum was below the main vessel and was separated from it by a distributor plate consisting of porous sintered metal (manufacturer and model or type describing its porosity). The top of the vessel was capped with a 2.54 cm ID gas exit port in the center of the top flange.

Heating/cooling coils were placed within the fluidized bed vessel. The coils, fabricated from copper tubing, consisted of both outer and inner rings. The outer coil was formed from 1.27 cm OD tubing wound in loops each having a diameter of 10 cm. The loops were separated from each other by 2.54 cm center to center. The overall

length of tubing in the outer coil was 4.5 m. An inner coil was manufactured from 0.97 cm OD copper tubing with loops of 5.08 cm. Loop spacing was 1.56 cm center to center and overall length was 2.97 m. During heating phases, heated mineral oil was passed through the coils to increase bed temperature. Cooling was accomplished by diverting the oil through coils immersed in a cooled water bath before directing it into the coils within the bed.

Exposure of the CO₂ was regulated using separate mass flow controllers (Alicat Scientific Type MC) for N₂ and CO₂ flows into the plenum; vapor flow was maintained using a Bronkhorst controlled evaporator mixer. CO₂ was measured in the exhaust stream using a Quantek Systems analyzer (model 902P).

Each nonisothermal desorption condition consisted of four phases: two prior and one following the desorption phase. The initial step was to heat or cool the sorbent bed to the target temperature under inert (N₂) gas flow. Once the desired bed temperature was achieved, then the adsorption phase was commenced. The bed was exposed to CO₂ concentrations of either 16.5 or 33% with 2% water vapor and the balance N₂. This flow and bed temperature was maintained until breakthrough occurred and the sorbent was saturated with CO₂. The next phase was nonisothermal desorption where the gas flows were maintained, but the bed was heated at a nearly constant rate by electrically heating the oil and circulating it within the bed through the heat exchange coils. This condition was maintained until a bed temperature of 110 °C was reached. The final phase was isothermal desorption using the same gas flow rate but replacing the CO₂ with N₂. The volumetric flow of CO₂ desorbed, $Q_{CO_2,des}$ was determined from the exit gas composition and input gas flow rates, %CO₂ and Q_{in} , respectively. From the overall mass balance the flow at the exit is equal to inlet flow plus that CO₂ flow released.

$$Q_{CO_2,des} = \frac{Q_{in}(\%CO_{2,out} - \%CO_{2,in})}{100 - \%CO_{2,out}} \quad (1)$$

Total flow into the process included CO₂, N₂, and water vapor. This convention results in a positive value when CO₂ is desorbed and is negative when CO₂ is adsorbed. The overall desorption of CO₂ was determined by integrating the flows over the duration of the experiment.

3. RESULTS AND DISCUSSION

Figure 3 shows the experimental CO₂ release at two different heating rate (1.87 and 2.5 K/min) for constant inlet CO₂ concentration (16.5%). It can be seen that CO₂ desorption from loaded immobilized PEI/silica sorbent increased monotonically with temperature. The curves in Figure 2 also present a slight dependence on the heating rate, being shifted toward

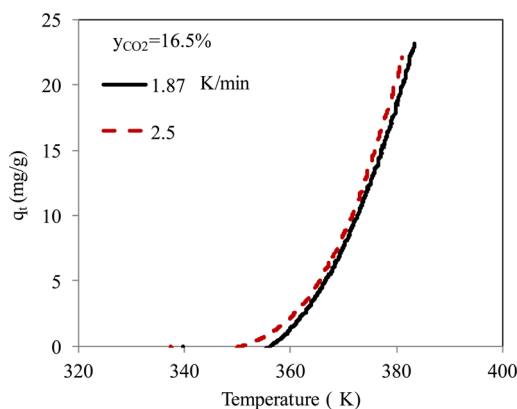


Figure 3. The temperature effect on CO₂ released for two different heating rates (1.87 and 2.5 K/min) using an inlet CO₂ concentration of 16.5%.

higher temperatures at lower heating rates. Though this effect was quite small it is not typical behavior, since the lower heating rate the sorbent spends longer time at a given temperature. During the adsorption experiments it was found that the adsorption rates were also atypical; the adsorption rates were slower at lower temperatures. The sorbent followed nucleation growth diffusion mechanisms and adsorption rates are thermodynamically limited at higher temperatures; the desorption rate exhibited a strong temperature dependence increasing sharply over this temperature range.^{4,18} The higher temperature in the fast heating rate experiment produced greater CO₂ in the early stages of the nonisothermal ramp.

Figure 4 shows the effect of inlet CO₂ concentration (16.5, 33%) on CO₂ released for constant heating rate. The inlet CO₂

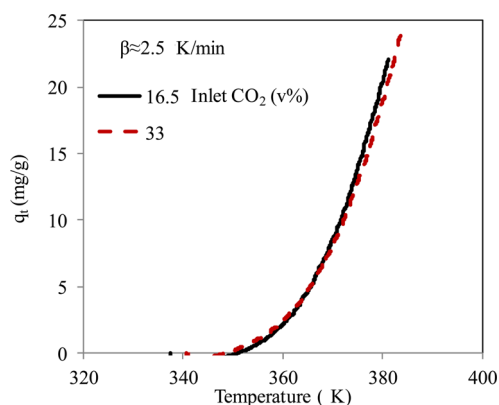


Figure 4. The temperature effects on CO₂ released for two different inlet CO₂ concentration (16.5 and 33%) using a constant heating rate (2.5 K/min).

concentration had slight or no effect on CO₂ release at 2.5 K/min. The equilibrium capacity of a similar PEI-based sorbent exhibited very little dependence over this range of CO₂ concentrations until the temperature reached 373 K.⁴ Likewise, the adsorption rates do not depend appreciably on CO₂ concentration at low temperatures.¹⁹

Kinetic Models. Kinetic analysis of thermally stimulated reactions is traditionally expected to produce an adequate kinetic description of the process in terms of the reaction model and of the Arrhenius parameters using a single-step kinetic equation

$$\frac{dX}{dt} = k(T)f(X) \quad (2)$$

where t is the time, T is the temperature, X is the extent of conversion, and $f(X)$ is the reaction model. In eq 2, $k(T)$ is the Arrhenius rate constant, which is given as

$$k(T) = A_a \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where R is the gas constant, and A_a and E_a are Arrhenius parameters, the pre-exponential factor and the activation energy, respectively. The reaction kinetics, eq 2, can be analytically integrated under isothermal conditions to yield

$$g(X) = \int_0^X \frac{dX}{f(X)} = k(T)t \quad (4)$$

where $g(X)$ is the integral form of the reaction model.

When the data are nonisothermal with constant heating rate ($\beta = dT/dt$), the time dependence of the above equations can be eliminated (eq 5).

$$\frac{dX}{dT} = \frac{dX}{dt} \frac{dt}{dT} = \frac{k(T)}{\beta} f(X) \quad (5)$$

Conventional kinetic analysis can be divided into two main categories:²⁰ those which employ data obtained under only one heating rate, and those based on performing a series of measurements under different heating rates (isoconversional methods). The first class of analytical methods enables Arrhenius parameters to be estimated by fitting kinetic data to assumed reaction models (Table 1). When applied to data obtained at a single heating rate, these methods produce highly uncertain values of the activation energy and of the pre-exponential factor, which are strongly correlated with each other.²¹ Isoconversional methods allow kinetic evaluation without making any assumptions about the analytical form of the reaction model.²² This approach assumes that the reaction rate at a constant conversion is only a function of temperature and that the reaction mechanism is not dependent on temperature or heating rate. These methods yield the activation energy as a function of the extent of conversion.^{23–25} Because estimating this sole dependence is sufficient for both making kinetic predictions and drawing mechanistic conclusions, the use of the isoconversional methods gives rise to completely model-free kinetic analysis.²² The main disadvantage of isoconversional methods is that they do not allow direct evaluation of the pre-exponential factor or reaction model.

Among the different isoconversional procedures reported in the literature, the differential isoconversional method suggested by Friedman (FR method) is used for the calculation of activation energies as a function of the extent of conversion.²³ Friedman's method implies that the basic nonisothermal kinetics equation may be written based on eq 5 as

$$\ln \left[\beta_i \left(\frac{dX}{dT} \right)_{X,i} \right] = \ln [A_X f(X)_i] - \frac{E_{a,X}}{RT_{X,i}} \quad (6)$$

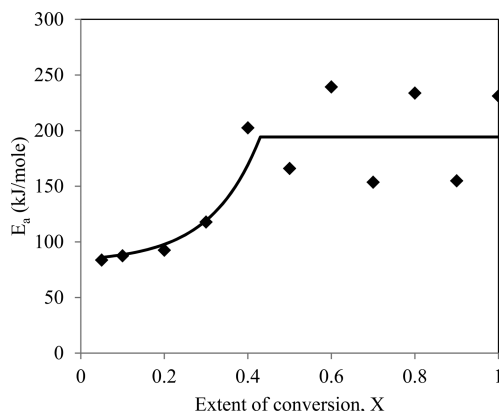
where β_i is the heating rate in the i^{th} test, $T_{X,i}$ is the temperature at a constant level of conversion in the i^{th} test, and $(dX/dT)_{X,i}$ is the temperature dependence on the conversion at a constant level of conversion in the i^{th} test. For a given level of conversion, X , the plot $\ln[\beta(dX/dT)]$ versus $(1/T)$ should be a

Table 1. Basic Kinetic Models and Properties of $f(X)$ and $g(X)$ Functions²⁷

no.	symbol	kinetic model	$f(X)$	$g(X)$
1	P1	Power Law	$4X^{3/4}$	$X^{1/4}$
2	P2		$3X^{2/3}$	$X^{1/3}$
3	P3		$2X^{1/2}$	$X^{1/2}$
4	P4		$2/3X^{-1/2}$	$X^{3/2}$
		Contraction Model		
5	R1	zero order	1	X
6	R2	2-D	$2(1-X)^{1/2}$	$[1-(1-X)^{1/2}]$
7	R3	3-D	$3(1-X)^{2/3}$	$[1-(1-X)^{1/3}]$
		Kinetics-Order Models		
8	F1	first order	$(1-X)$	$-\ln(1-X)$
9	F3/2	3/2 order	$(1-X)^{3/2}$	$2[(1-X)^{-1/2}-1]$
10	F2	second order	$(1-X)^2$	$(1-X)^{-1}-1$
11	F3	third order	$(1-X)^3$	$1/2[(1-X)^{-2}-1]$
		Nucleation Model		
12	A3/2	$n = 1.5$	$3/2(1-X)[- \ln(1-X)]^{1/3}$	$[- \ln(1-X)]$
13	A2	$n = 2$	$2(1-X)[- \ln(1-X)]^{1/2}$	$[- \ln(1-X)]$
14	A3	$n = 3$	$3(1-X)[- \ln(1-X)]^{2/3}$	$[- \ln(1-X)]$
15	A4	$n = 4$	$4(1-X)[- \ln(1-X)]^{3/4}$	$[- \ln(1-X)]$
		Diffusion Model		
16	D1	1-D	$1/(2X)$	X^2
17	D2	2-D	$1/[- \ln(1-X)]$	$(1-X)\ln(1-X)+X$
18	D3	3-D (Jander)	$(3/2)(1-X)^{2/3}[1-(1-X)^{1/3}]$	$[1-(1-X)^{1/3}]^2$
19	D4	3-D (Grinstling)	$(3/2)[(1-X)^{-1/3}-1]$	$(1-2X/3)-(1-X)^{2/3}$

straight line whose slope can be used to evaluate the apparent activation energy.

The nonisothermal desorption kinetics of CO₂ from immobilized polyethylenimine was analyzed by a differential isoconversional method using eq 6. Figure 5 illustrates the

**Figure 5.** The activation energy, E_a , as a function of the extent of conversion, X , for CO₂ desorption of CO₂-loaded immobilized polyethylenimine (PEI) on mesoporous silica under nonisothermal conditions.

variation of the apparent activation energy, E_a , as a function of the extent of conversion. The apparent activation energy, E_a , increased rapidly in the conversion range of $0.05 \leq X \leq 0.3$ with extent of conversion, X , and after this range ($X \geq 0.3$), the increase continued approximately linearly. According to Vyazovkin²² increases in activation energy corresponds to a kinetic scheme with competing reactions, although some independent and consecutive reactions may also give such a dependence.²¹ Therefore, the initial increase in apparent activation energy as conversion progress could be explained by competition between adsorption and desorption taking place in the presence of CO₂. The initial increase in apparent activation energy with conversion suggests that adsorption and desorption both contribute to the total heat release in the early stages of the process.

In the conversion range of 0.3 to 0.95, the E_a was independent of the extent of conversion, which was indicative of single-stage character of an irreversible process.²⁷ All of the tested CO₂ levels and heating rates were originally included in the generation of the isoconversion plot (Figure 5) on the basis that there was no significant difference that could be attributed to these parameters. Six outliers were identified out of the 60 data points included by considering the leverage that each data point exerted on the resulting activation energies. Data points yielding unrealistic activation energies were excluded from the results. These outliers were found in the middle range of conversion levels between 30 and 60%. This does not explain the range of scatter displayed in Figure 5 at the higher conversion levels. The variation may be a numerical artifact of the Friedman approach where the experimental data of conversion versus temperature was fitted directly using a polynomial expression which was then differentiated to obtain dX/dT (eq 6). In any case, the E_a was considered constant in this region, and desorption can be modeled using a single-step reaction mechanism irrespective of heating rate.

The normalized conversion (X) was typically calculated from the corresponding CO₂ release from fluid bed as

$$X = \frac{q_t}{q_c} \quad (7)$$

where q_t represents the accumulated CO₂ release at arbitrary time t (or temperature T), and q_c is the total CO₂ released at the end of the CO₂ desorption process.

Process Model Identification. In order to analyze the kinetics of the desorption process, model fitting was performed in the conversion region where the apparent activation energy was approximately constant and a single-step reaction model could be used. The nonisothermal kinetic data for CO₂ desorption were fitted to each of the 19 reaction models listed in Table 1. The Arrhenius parameters of CO₂ desorption were calculated for the overall process at a given heating rate using eq 6 after rearrangement²⁶

$$\ln \left[\frac{\beta \left(\frac{dX}{dT} \right)}{f_j(X)} \right] = \ln A_j - \frac{E_{a,j}}{RT} \quad (8)$$

where $f_j(X)$ is a differential form (Table 1), and $\ln A_j$ and $E_{a,j}$ are the pairs of Arrhenius parameters obtained for the j^{th} reaction model. Varying the different $f_j(X)$ models, from eq 8 for the best chosen reaction model (Table 1), the Arrhenius parameters ($\ln A_j$, $E_{a,j}$) of the investigated process were calculated. Two models were able to describe the experimental

desorption rate data adequately – the two-dimensional diffusion model (D2) and the zero order reaction model (R1). While several models were able to fit some of the desorption data well, only models D2 and R1 explained more than 98% of the variance for every test condition at the 95% confidence interval. The best reaction model for CO₂ desorption on this PEI sorbent was the two (2) dimensional diffusion (bidimensional shape), D2, because this model had the highest overall variance explained ($R^2 > 99\%$).

The method of invariant kinetic parameters²⁷ was applied to evaluate the accuracy of the two potential reaction models (D2 and R1) for obtaining the activation energy and pre-exponential factor. This method makes use of the so-called “compensation effect”. The “compensation effect” is observed when a model fitting method is applied to a single-heating rate experiment. The “compensation effect” is a pattern of kinetic behavior recognized within groups of related heterogeneous reactions or catalyst. The compensation effect (or the “ θ rule”) was investigated using^{28–32}

$$\ln A_j = a + bE_{a,j} \quad (9)$$

where subscript j refers to one of the possible reaction models $f_j(X)$ assumed to describe the process. Equation 9 represents the artificial isokinetic relationship (IKR). The parameters of eq 9 are $a = \ln k_{iso}$ (an artificial isokinetic rate constant) and $b = 1/RT_{iso}$ (R is the gas constant and T_{iso} is an artificial isokinetic temperature).

Using this method the values for T_{iso} were independently calculated for each model and compared to the range of the experimental conditions (340–380 K). The values for T_{iso} from two-dimensional diffusion model (D2) were within the experimental test conditions. On the other hand, the estimated values for T_{iso} from the zero order decomposition rate model, R1, were not. The upper T_{iso} for R1 was 406 K. Furthermore, it will be shown that the artificial isokinetic reaction constant for model D2 was consistent with the measured desorption rates and equilibrium constants as estimated in the literature, while the rate constant for model R1 was not.

It is also noted that a similar PEI sorbent adsorbs CO₂ according to a nucleation growth diffusion process.⁴ Monazam et al. found that the nucleation growth adsorption follows a diffusion process which was characterized by a shape factor of 2 indicative of a two-dimensional diffusion process. They went on to conjecture that the shape factor was a result of non-spontaneous adsorption within rod-shaped pores of a heterogeneous nature at low temperatures. It is logical that the reverse process, i.e. desorption of CO₂, from the same surface pore structure would likewise follow a 2D diffusion process. For these reasons the CO₂ desorption from this PEI sorbent was further characterized using the 2-dimensional diffusion model, D2.

The calculated Arrhenius parameters are presented in Table 2 for the two-dimensional diffusion model (D2) for CO₂ desorption at every heating rate and gas concentration studied over the conversion range of $0.05 \leq X \leq 0.98$. Initially the analysis included the data over the range $0.3 \leq X \leq 0.95$, where approximately constant activation energy was found; however, including the entire range did not significantly alter the results and improved the variance explained. The heating rates were varied from 1.06 to 2.65 K/min during the nonisothermal ramp of the sorbent up to final regeneration temperature. The average value for $\ln A$ was 71.3 ± 3.6 , while E_a was 230.5 ± 10.6 kJ/mol. The uncertainty is reported from the 95% confidence

Table 2. Arrhenius Parameters ($\ln A$, E_a) and CO₂ Released of Nonisothermal CO₂ Desorption of CO₂-Loaded Immobilized Polyethylenimine (PEI) on Mesoporous Silica Obtained by Eq 8 and Corresponding Best Fit Reaction Models (for $0.05 \leq X \leq 0.99$)

CO ₂ (mole %)	β (K/min)	CO ₂ release (mg/g)	model Table 1	$\ln A$	E_a (kJ/mol)	R^2
16.5	1.06	42.70	D2	63.44	207.81	0.9918
16.5	1.87	23.08	D2	73.67	238.02	0.9932
16.5	2.14	27.27	D2	69.12	223.48	0.9928
16.5	2.5	23.38	D2	77.68	248.77	0.9967
16.5	2.62	27.62	D2	68.59	221.57	0.9944
33%	2.06	25.01	D2	74.24	239.37	0.9958
33%	2.4	24.27	D2	70.37	227.25	0.9977
33%	2.655	23.39	D2	73.73	237.76	0.9955

interval over all test conditions. The experimental observed desorption kinetic rates can be reported as

$$k_d = 9.7 \times 10^{30} e^{-\frac{230500}{RT}} \quad (10)$$

where k_d is the desorption rate constant, min^{-1} . The apparent activation energies (E_a) for this reaction model (Table 2) were in good agreement with values of E_a obtained by different isoconversional methods for $0.4 \leq X \leq 0.6$ (Figure 5). From eq 10 it can be readily shown that the desorption rates increased from 0.01 up to 0.34 min^{-1} between 90 and 110 °C. Thus, desorption was slower than the adsorption; the adsorption rate for the same sorbent in a fluidized bed is reported¹⁷ to be 0.53 min^{-1} at 40 °C and 15% CO₂. This indicates that the desorption process may require substantially longer reaction times than the corresponding adsorption process depending on the concentrations of CO₂ in the flue gas.

The artificial isokinetic parameters for the CO₂ desorption process was obtained for this model (D2) from eq 9. Figure 6

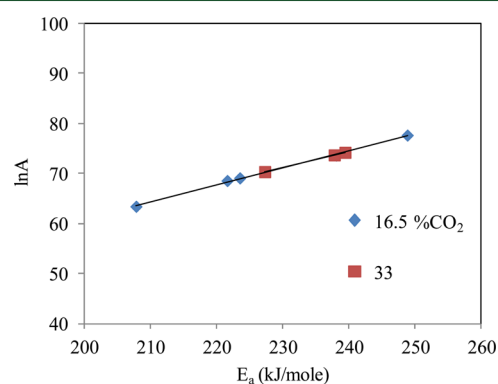


Figure 6. The isokinetic relationships ($\ln A$ vs E_a) obtained for CO₂ desorption of CO₂-loaded immobilized polyethylenimine (PEI) on mesoporous silica at different heating rates and CO₂ concentrations.

shows this relationship over the different heating rates and inlet CO₂ concentrations. The expression shows a straight line fit to all of the test points consistent with eq 9. Table 3 shows the results for correlation parameters a and b , as well as the k_{iso} and T_{iso} values for the two-dimensional diffusion model (D2). The rate constant k_{iso} matches those values obtained using eq 10 for each given T_{iso} .

Knowing the activation energies at each level of conversion allows one to estimate the corresponding pre-exponential

Table 3. Isokinetic Parameters (a , b , k_{iso} , and T_{iso}) of Eq 9 Obtained for the Best Reaction Model (D2 in Table 1) for CO₂ Desorption of CO₂-Loaded Immobilized Polyethyleneimine (PEI) on Mesoporous Silica

CO ₂ (mole %)	a (min ⁻¹)	b (mol/kJ)	k_{iso} (min ⁻¹)	T_{iso} (K)	R^2
16.5	-7.3623	0.3416	0.00063	352.1	0.9983
33.0	-2.1188	0.319	0.12018	377.1	1

factors. Once the correlation parameters a and b have been evaluated, the $E_{a,X}$ values were substituted for $E_{a,j}$ in eq 9 to estimate the corresponding $\ln A_X$ values and obtain the dependence of $\ln A_X$ on X . Figure 7 shows the variation of the $\ln A_X$

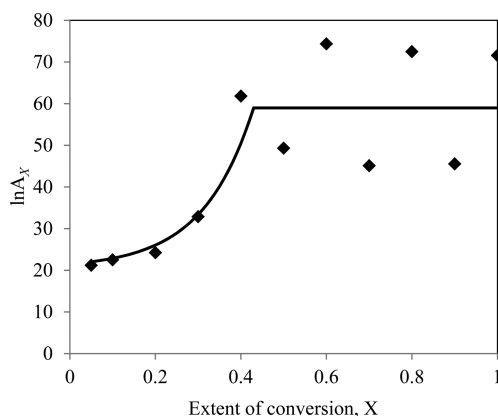


Figure 7. Dependence of the $\ln A_X$ on the extent of conversion, X , for CO₂ desorption of CO₂-loaded immobilized polyethyleneimine (PEI) on mesoporous silica estimated from eq 9.

A_X as a function of the extent of conversion X for CO₂ desorption process of immobilized polyethyleneimine (PEI). The values of $\ln A_X$ had similar dependence on X as the apparent activation energies in Figure 5.

Thermodynamic Analysis. In order to evaluate the thermodynamics of CO₂ sorption on PEI-based sorbents, the Langmuir isotherm is commonly assumed. It is recognized that the Langmuir isotherm does not fit the test data for this system at low temperatures; however, at high temperatures where desorption is prevalent both Langmuir and Dubinin–Radushkevich isotherms worked well for adsorption.⁴ Langmuir considered the adsorption and desorption of single reaction expressed as



where S is the solid surface with nothing on it, G is the compound in the gaseous phase, and SG is the solid surface with gaseous compound on it. The rate of gas adsorption to the solid is proportional to a driving force times an area. The driving force is the concentration in the gas, and the area is the amount of unoccupied active surface. If the fraction of covered surface is X , the rate of adsorption per unit of surface is

$$\frac{dX_{ads}}{dt} = k_a C(1 - X) \quad (12)$$

Then the rate of desorption is proportional to the amount of surface is covered:

$$\frac{dX_{des}}{dt} = k_d X \quad (13)$$

The overall rate equation is

$$\frac{dX}{dt} = k_a C(1 - X) - k_d X \quad (14)$$

For high initial gas concentration eq 13 can be written as³³

$$\frac{dX}{dt} = k_a C_0 - (k_a C_0 + k_d)X \quad (15)$$

By defining the equilibrium constant as $K = k_a/k_d$, at equilibrium $dX/dt = 0$, so eq 14 becomes³³

$$\frac{1}{X_e} \cong \frac{KC_0 + 1}{KC_0} \quad (16)$$

For example, at a temperature of 100 °C the equilibrium constant, K , was estimated to be 17.3 cc CO₂/mg sorbent based upon k_a of 840 cc/g·min¹⁷ and k_d of 0.05 min⁻¹ based upon the average kinetic parameters from Table 2 or eq 10. This compared favorably with the value of 9.6 cc/mg reported for similar sorbent having PEI content of 50%.⁴ However, at temperatures of 80 °C the equilibrium constant from the ratio of measured rates, k_a/k_d , did not agree with the Langmuir model, 1420 and 22.7 cc/mg, respectively. This demonstrates the danger of using surface reaction kinetics and associated thermodynamic analysis to these diffusion controlled processes.

4. CONCLUSIONS

Desorption of CO₂ from CO₂-loaded immobilized polyethyleneimine (PEI) on mesoporous silica was studied in a temperature controlled fluidized bed reactor. Desorption rates under nonisothermal conditions were analyzed by model-free and model-fitting approaches. The model-free approach as represented by the nonisothermal isoconversional methods revealed that for $0 \leq X \leq 0.3$ desorption of CO₂ was complex and probably involved a combination of several processes. However, in the range of $0.3 \leq X \leq 0.95$ the apparent activation energy was approximately constant indicating a single step rate controlling desorption process. Desorption rates were found to increase from 0.006 up to 0.337 min⁻¹ between 90 and 110 °C. This is the first measured desorption kinetic study for PEI based sorbents reported in the literature.

The Arrhenius parameters by model-fitting methods were in good agreement with values of E_a and $\ln A$ obtained by isoconversional methods. Desorption rates were fitted best using either the two-dimensional diffusion model (D2) or the zero order reaction model (R1). The accuracy of the kinetics parameters from the model fitting was tested using the method of invariant kinetic parameters. Artificial isokinetic temperatures (T_{iso}) were compared for different heating rates and inlet CO₂ concentrations for each of these models. Only the T_{iso} values for model D2 were found to be within the range of experimental temperatures employed. This indicated that the two-dimensional diffusion model (D2) was properly chosen for conversions $X \geq 0.30$. In addition, the artificial isokinetic rate constants agreed closely to the rates from D2 obtained from the model fitting method.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 304-285-4647. Fax 304-285-4403. E-mail: lshadl@netl.doe.gov.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the Department of Energy for funding the research through the Fossil Energy's Carbon Sequestration/CO₂ Capture Research program.

■ REFERENCES

- (1) Aaron, D.; Tsouris, C. *Sep. Sci. Technol.* **2005**, *40*, 321–348.
- (2) Notz, R.; Asprion, N.; Clausen, I.; Hasse, H. *Chem. Eng. Res. Des.* **2007**, *85* (4), 510–515.
- (3) Zhang, P. A.; Xiao, P. *Energy Convers. Manage.* **2008**, *49*, 346–356.
- (4) Monazam, E. R.; Shadle, L. J.; Miller, D. C.; Pennline, H. W.; Fauth, D. J.; Hoffman, J. S.; Gray, M. L. *AIChE J.* **2012**, DOI: 10.1002/aic.13870.
- (5) Monazam, E. R.; Shadle, L. J.; Siriwardane, R. V. *AIChE J.* **2011**, *57*, 3153–3159.
- (6) Monazam, E. R.; Shadle, L. J.; Siriwardane, R. V. *Eng. Chem. Res.* **2011**, *50*, 10989–10995.
- (7) Heydari-Gorji, A.; Belmabkhout, Y.; Sayari, A. *Langmuir* **2011**, *27*, 12411–12416.
- (8) Aziz, B.; Zhao, G. Y.; Hedin, N. *Langmuir* **2011**, *27*, 3822–3834.
- (9) Yan, X. L.; Zhang, L.; Zhang, Y.; Yang, G. D.; Yan, Z. F. *Ind. Eng. Chem. Res.* **2011**, *50*, 3220.
- (10) Belmabkhout, Y.; Sayari, A. *Adsorption* **2009**, *15*, 318–328.
- (11) Yue, M. B.; Chun, Y.; Cao, Y.; Dong, X.; Zhu, J. H. *Adv. Funct. Mater.* **2006**, *16*, 1717–1722.
- (12) Hicks, J. C.; Drese, J. H.; Fauth, D. J.; Gray, M. L.; Qi, G. G.; Jones, C. W. *J. Am. Chem. Soc.* **2008**, *130*, 2902–2903.
- (13) Couck, S.; Denayer, J. F. M.; Baron, G. V.; Remy, T.; Gascon, J.; Kapteijn, F. *J. Am. Chem. Soc.* **2009**, *131*, 6326–6327.
- (14) Vaidhyanathan, R.; Iremonger, S. S.; Dawson, K. W.; Shimizu, G. K. H. *Chem. Commun.* **2009**, 5230–5232.
- (15) Gibbins, J. R.; Crane, R. I.; Lambropoulos, D.; Booth, C.; Roberts, C. A.; Lord, M. *Greenhouse Gas Control Technol.* **2005**, *7*, 139–146.
- (16) Zhen, W.; Mengxiang, F.; Yili, P.; Shuiping, Y.; Zhongyang, L. *Chem. Eng. Sci.* **2013**, *93*, 238–249.
- (17) Monazam, E. R.; Spenik, J.; Shadle, L. J. *Chem. Eng. J.* **2013**, *223*, 795–805.
- (18) Xu, X.; Song, C.; Andrésen, J. M.; Miller, B. G.; Scaroni, A. W. *Microporous Mesoporous Mater.* **2003**, *62*, 29–45.
- (19) Sayari, A.; Belmabkhout, Y.; Serna-Guerrero, R. *Chem. Eng. J.* **2011**, *171*, 760–774.
- (20) Vyazovkin, S. *Anal. Chem.* **2004**, *76*, 3299–3312.
- (21) Vyazovkin, S.; Wight, C. A. *Thermochim. Acta* **1999**, *53*, 340–341.
- (22) Vyazovkin, S. *Int. J. Chem. Kinet.* **1996**, *28*, 95–101.
- (23) Friedman, H. J. *Polym. Sci.* **1963**, Part C 6, 183–195.
- (24) Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1881–1886.
- (25) Flynn, J. H.; Wall, L. A. *J. Res. Natl. Bur. Stand.* **1966**, Sect. A 70, 487–523.
- (26) Vyazovkin, S.; Linert, W. *Int. J. Chem. Kinet.* **1995**, *27*, 73–84.
- (27) Janković, B.; Adnađević, B.; Jovanović, J. *Thermochim. Acta* **2007**, *452*, 106–115.
- (28) Lesnikovich, A. I.; Levchik, S. V. *J. Therm. Anal.* **1983**, *27*, 89–93.
- (29) Agrawal, R. K. *J. Therm. Anal.* **1986**, *31*, 73–86.
- (30) Agrawal, R. K. *J. Therm. Anal.* **1989**, *35*, 909–917.
- (31) Vyazovkin, S. V.; Lesnikovich, A. J.; Romanovsky, I. S. *J. Therm. Anal.* **1988**, *34*, 609–618.
- (32) Klinar, D.; Golob, J.; Krajnc, M. *Acta Chim. Slov.* **2003**, *50*, 473–489.
- (33) Azizian, S. J. *Colloid Interface Sci.* **2004**, *276*, 47–52.