Development of K and N Based Composite CO₂ Sorbents (KN) Dried with a
Supercritical Fluid

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ABSTRACT

The objective of this research was to develop composite CO₂ sorbents for
overcoming the shortcomings of the corresponding individual sorbents. The
composite sorbents were synthesized with K₂CO₃, 3-aminopropyltriethoxysilane
(APTES) and tetraethylorthosilicate (TEOS) and dried either with a supercritical or
conventional technique. Comparative experiments demonstrated that supercritical
fluid drying (SCFD) was better than conventional drying (CD) in preparing CO₂
sorbents with more developed pore structure and thus higher CO₂ sorption capacity.

The composite sorbent prepared with SCFD was tested under various conditions for

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their effects on CO₂ sorption capacity. The optimal K:N mole ratio for preparation of the composite sorbent and the reaction conditions for achieving the highest sorption capacity were obtained. In addition, the sorbent proved to be regenerable. Thus, supercritical drying is an effective technique for preparation of a promising composite CO₂ sorbent.

Keywords: Post-combustion, CO₂ capture, Sorption, Amine, K₂CO₃, Supercritical fluid drying

INTRODUCTION

Climate change reportedly associated with the increase in atmospheric CO₂ concentration is one of the key challenges people have to face in the 21st century [1-3]. Coal is one of the major energy resources in the world and it makes great contributions to gross domestic product [4]. For many years, combustion has been the dominant way of coal utilizations for different purposes including electricity generation, which has results in huge CO₂ emissions into the atmosphere. Therefore, capturing the CO₂ emitted from coal-fired power plants is necessary.

Several types of post-combustion CO₂ capture technologies including sorption and membrane have been developed and great progresses have been made in these areas in recent years [5-8]. Sorption is a promising choice since the technology is more applicable to the flue gas which has high flow rates, low pressures and low CO₂ concentrations [8]. The sorbents so far developed are purely either inorganic or

organic. Supported K_2CO_3 and Na_2CO_3 are the representatives of inorganic sorbents and their CO_2 capture reactions are:

The carbonates are inexpensive and widely available, and thus people are increasingly interested in using them for CO_2 capture. Organic sorbents are based on amine compounds. People have loaded different types of amine compounds such as ethylenediamine and polyetherimide onto various supporting materials including titanium oxide and silica for syntheses of sorbents [9-11]. All the amine based CO_2 sorption technologies are realized using either

or

Both inorganic and organic sorbents have their own advantages and shortcomings. Inorganic sorbents are relatively inexpensive and stable but their CO_2 sorption and desorption rates are slow. Organic sorbents typically have higher CO_2 sorption capacities and are more dynamic during sorption and desorption processes than their inorganic counterparts [12, 13]. For example, the CO_2 sorption capacity of the polyethylenimine-loaded mesoporous carbons prepared by Wang and his coworkers was as high as 4.82 mmol- CO_2 /g-sorbent [12]. However, the sorbent degradation or amine loss issue, which leads to the decreases in CO_2 sorption capacities of organic sorbents during cyclic operations, has not been resolved [14]. To

take the advantages of both types of sorbents and overcome their shortcomings, this research was designed to develop a composite CO₂ sorbent synthesized with an amine-containing compound and K₂CO₃. In addition, supercritical fluid and conventional drying approaches were compared for their effects on the performances of the resulting sorbents.

EXPERIMENTS

Sorbent preparation and characterization

The chemicals needed for preparing the sorbents used in this research were 3-aminopropyltriethoxysilane (APTES, ALDRICH, 99.0%), Tetraethylorthosilicate (TEOS, ALDRICH, 98.0%), ethanol (C₂H₅OH, Decon Labs, Inc., 200-proof), and pure K₂CO₃ (EMD Chemical Inc., 99.0%). All the composite sorbent preparation processes proceeded through gel formation and drying processes. Gel formations were realized by mixing TEOS, 28.6 wt-% K₂CO₃ solution, APTES and ethanol with various mole ratios of K:N at room temperature for 10 to 15 mins, depending on the mole ratio of the raw material. The quantities of TEOS and ethanol used in each sorbent preparation are constant. Conventional and supercritical methods were used to dry the gels. The conventional drying (CD) was realized with an oven at 80°C. Supercritical fluid drying(SCFD) started with aging wet gels at room temperature for 1 hr, followed by soaking them in pure C₂H₅OH three times to remove water at room temperature, drying them within a supercritical apparatus, a Speed SFE system

(Applied Separations, Inc., Allentown, PA) under 10.0 MPa at room temperature to eliminate their C₂H₅OH until no noticeable C₂H₅OH exited from the supercritical apparatus, then dry them for 5 hrs under the same pressure but at a little higher temperature, 31 °C. The resulting sorbents from the conventional and supercritical fluid drying methods were named as CD-KN and SCFD-KN, respectively. In addition, for comparison purpose, a N-containing sorbent, designated as SCFD-N, was prepared with 3.75:7.5:75:14.75 mole ratio of TEOS, APTES, deionized water and ethanol and dewatered with SCFD technique.

The prepared KNs were characterized with different methods. A Micrometrics TriStar 3000V 6.04 A BET (Brunauer, Emmet, and Teller) analyzer was used for determination of the surface areas and the pore structures of KNs. Fourier transform infrared (FT-IR) spectra of SCFD-N (the N-containing sorbent synthesized with APTES and TEOS under supercritical fluid drying condition), K₂CO₃, and fresh and spent KNs were collected using a Thermo Nicolet Magna-IR 760 spectrometer. The morphological analyses of KNs were conducted using an FEI Quanta FEG 450 field-emission scanning electron microscope (SEM). In addition, a Physical Electronics PE5800 X-ray photoelectron spectrometer (XPS) was also used to characterize the sorbents.

Apparatus and operation

The experimental apparatus used in this research for CO₂ sorption and desorption has been reported elsewhere [15]. 0.1~0.5 g KN was used for each

sorption test, depending on the density of the sorbent. A 3/8 in. quartz tube with a notch in it was used as the sorption/desorption reactor. Two pieces of quartz wool were placed at the two sides of the sorbent bed to hold sorbent during sorption and sorbent regeneration. Sorption temperatures in the reactor were controlled by a F21135 tube furnace (Barnstead International, Dubuque, IA). Water in the post-adsorption gas stream was eliminated by a water removal unit prior to CO₂ analysis. CO₂ concentrations of the inlet/outlet gas stream were measured by a ZRE infrared gas analyzer (Fuji Electric System Co., Ltd., Tokyo, Japan), and sorption and desorption data were collected with a DataChart 3000 recorder (Monarch Instrument, Inc., Amherst, NH).

Each sorption test was started with heating the reactor or adsorber loaded with a sorbent to 150 °C within a 500 ml/min N₂ environment to purge the moisture and CO₂ in the reactor, followed by cooling the reactor to a desired sorption temperature, then passing a simulated flue gas stream with 1 vol-% CO₂ and 1 vol-% H₂O. Each CO₂ sorption test was ended when the outlet CO₂ concentrations reached 1 vol-%. CO₂ desorption was performed with pure N₂ and stopped when the CO₂ reading on the gas analyzer was zero. Each test was conducted three times under the same reaction condition, and the reported result at a given data point is the average value.

RESULTS AND DISCUSSION

Characteristics of KNs

The FTIR spectra of SCFD-N, K_2CO_3 , and two KNs with different K:N mole ratios are presented in Figure 1. The FTIR spectra of pure amine and K_2CO_3 , as shown in Figures 1a and 1b, respectively, well match with those reported in literature [16, 17]. The strong bands at 1050 cm^{-1} in Figure 1c are due to the C-N stretch of alkyl group or the presence of strained Si-O-Si bonds [18]. The bands at $690\sim 880\text{ cm}^{-1}$ result from N-H stretches. With Figures 1a and 1b being references, there are three new bands at 1585 cm^{-1} , 1506 cm^{-1} and 1380 cm^{-1} in Figures 1c and 1d. They are associated with N-C=O resulting from the APTES and K_2CO_3 mixing process [19, 20]. The band at 1390 cm^{-1} in Figure 1d is stronger than that in Figure 1c, which may be caused by the increase in K_2CO_3 loading, however, it is still weaker than its counterpart in Figure 1b obtained with pure K_2CO_3 .

Advantages of SCFD as a CO_2 sorbent dewatering approach

The elemental analyses of the two sorbents prepared with the same materials, 10 mL TEOS, 10 mL 26.8 wt-% K_2CO_3 , 30 mL APTES, and 20 mL ethanol (TEOS: K: N: ethanol = 3.75:5:11.25:14.75)] but by two different drying methods were measured with XPS. The K and N concentrations of the CD-KN were found to be 3.5 mmol-K/g-KN and 5.51 mmol-N/g-KN, respectively, while the corresponding values of SCFD-KN are 3.98 mmol-K/g-KN and 6.59 mmol-N/g-KN.

The pore volume and BET surface areas of the CD-KN are $0.02\text{ cm}^3/\text{g}$ and $6.90\text{ m}^2/\text{g}$, respectively, much smaller than those corresponding values of SCFD-NK, $0.176\text{ cm}^3/\text{g}$ and $72.2\text{ m}^2/\text{g}$, while the pore size of the CD-KN, 15.0 nm, is much larger than

that of SCFD-KN, 3.1 nm. The higher pore volume, and surface area, and smaller pore size of SCFD-NK are all beneficial to the improvement of its CO₂ sorption capacity. The SEM images of the same CD-KN and SCFD-KN (Figure 2) demonstrate that the SCFD-KN is more unfragmented and porous than the CD-KN. Therefore, SCFD is an effective method for the improvement of the pore structure of the sorbent.

The CO₂ sorption profiles of the CD-KN and SCFD-KN are shown in Figure 3. The CO₂ sorption capacity of the SCFD-KN, 2.03 mmol-CO₂/g-KN, is much higher than that (1.17 mmol-CO₂/g-KN) achieved with the CD-KN. The better CO₂ sorption performance of the SCFD-KN should be attributed to its superior structure, including higher BET surface area and larger pore volume as well as smaller pore size and diffusion for the gas phase, its netlike assembly, and higher K and N concentrations.

In addition, the null-experiments were conducted. The CO₂ sorption capacity of the pure amine-silica sorbent is 1.49 mmol CO₂/g sorbent while that of pure K₂CO₃ is 0.041 mmol CO₂/g sorbent [21]. Therefore, the CO₂ sorption performance of the composite sorbent is better than individual sorbents and a simple mixture of them.

Factors affecting the performance of SCFD-KNs

K and N loadings

The observed CO₂ sorption capacities of the composite sorbents are mainly determined by their K and N loadings or concentrations. Theoretically, all the K and N on the surface of a given sorbent can be used for CO₂ sorption via R1 and R3.

However, the theoretical sorption capacities are not reachable because the molecular sizes of the sorption products are almost always larger than those of sorbents. Furthermore, the size of $[-NH_3]^+[-NHCO_2]^-$ formed with R3 is larger than that of $KHCO_3$ generated from R1. Therefore, it is desired that more K in form of K_2CO_3 is loaded on SCFD-KN with a given surface area to maximize the CO_2 sorption capacities of the composite sorbents. However, the activation energy of CO_2 sorption with $-NH_2$ (E_{R3} , 49.0 kJ/mol), is smaller than that with K_2CO_3 (E_{R1} , 71.9 kJ/mol) [22,23]. Based on

$$\frac{k_{R1}}{k_{R3}} = \frac{A_{R1}}{A_{R3}} e^{\frac{E_{R3}-E_{R1}}{8.314T}} = \frac{A_{R1}}{A_{R3}} e^{\frac{229.00}{8.314T}} = \frac{A_{R1}}{A_{R3}} e^{\frac{2.75434}{T}} \quad E1$$

where k_{R1} and k_{R3} are the rate constants of the forward reactions of R1 and R3, respectively, while A_{R1} and A_{R3} are the corresponding pre-exponential factors of Arrhenius forms of the forward reactions of R1 and R3, at 40 °C (313 K),

$$\frac{k_{R1}}{k_{R3}} = \frac{A_{R1}}{6,632.9 \times A_{R3}} \quad E2$$

Thus it is very likely that the CO_2 sorption rate of R3 is larger than that with R1 assuming that A_{R1} and A_{R3} are too different. In addition, the reaction orders of all the associated chemicals in both R1 and R3 affect the rates of CO_2 sorption with the sorbent. The total CO_2 sorption rate of the composite sorbent can be expressed as

$$-\frac{dc_{CO_2}}{dt} = k_{R1} c_{K_2CO_3, R1}^{n_{K_2CO_3, R1}} c_{CO_2, R1}^{n_{CO_2, R1}} c_{H_2O, R1}^{n_{H_2O, R1}} - k_{-R1} c_{KHCO_3, -R1}^{n_{KHCO_3, -R1}} + k_{R3} c_{-NH_2, R3}^{n_{-NH_2, R3}} c_{CO_2, R3}^{n_{CO_2, R3}} c_{H_2O, R3}^{n_{H_2O, R3}} - k_{-R3} c_{[-NH_3]^+[-HCO_3]^-}^{n_{[-NH_3]^+[-HCO_3]^-}} c_{-R3}^{n_{-R3}} \quad E3$$

where, $c_{K_2CO_3}$, c_{CO_2} , c_{H_2O} , c_{KHCO_3} , c_{-NH_2} and $c_{[-NH_3]^+[-HCO_3]^-}$ are the concentrations of K_2CO_3 , $KHCO_3$, CO_2 , H_2O , $-NH_2$, and $(-NH_3^+)(-HCO_3^-)$ at any sorption time, t,

respectively, k_{R1} , k_{-R1} , k_{R3} and k_{-R3} are the corresponding rate constants of
 forward and reverse processes of R1 and R3, while $n_{K_2CO_3, R1}$, $n_{CO_2, R1}$, $n_{H_2O, R1}$, $n_{KHCO_3, -R1}$,
 $n_{-NH_2, R3}$, $n_{CO_2, R3}$, $n_{H_2O, R3}$ and $n_{[-NH_3]^+[-HCO_3]^- , -R3}$, are the reaction orders with respect to
 K_2CO_3 , CO_2 , H_2O , $KHCO_3$, $-NH_2$, CO_2 , H_2O and $(-NH_3^+)(-HCO_3^-)$ in the reversible
 R1 and R3. The loadings of K and N of SCFD-KNs affect the pre-exponential factors
 of the Arrhenius equations and thus the rate constants, and the concentration terms in
 E3, which eventually affect the total CO_2 sorption capacities of the composite
 sorbents as presented in Figure 4. The CO_2 sorption capacity changes significantly
 within the tested K:N ratio range, and reaches the highest value, 2.83
 mmol- CO_2 /g-KN when the K:N ratio is 6:12 or 1:2. High K and N loadings did not
 necessarily lead to high CO_2 sorption capacity due to the decrease in surface area and
 pore-clogging, as indicated in Table 1. The lower the loadings of K and N on the
 surface of the SCFD-KN, the higher the BET surface area and pore volume of the
 sorbent are and the lower the average pore size of the sorbent is. The sorbent with the
 lowest K (0.024 mole K) and N (0.034 mole N) loadings has the highest BET surface
 area and pore volume and the lowest pore size. Neither K and N loadings nor the pore
 characteristics can be used as the sole indicator of CO_2 sorption performances of
 SCFD-KNs. The CO_2 sorption capacity of SCFD-KN is the integral effect of both
 pore characteristics and K as well as N loadings. Therefore, the SCFD-KN with the
 highest CO_2 sorption capacity (TEOS: K: N: ethanol = 3.75:6:12:14.75) is chosen for
 further studies.

Temperature

The CO₂ sorption processes of SCFD-KN or the forward reactions of R1 and R3 are relatively sensitive to temperatures because neither E_{R1} nor E_{R3} is too low. However, K based CO₂ sorption is more sensitive to temperature than N based sorption because of

$$\frac{d[k_{R1}/k_{R3}]}{dT} = \frac{A_{R1}}{A_{R3}} e^{\frac{2,754.34}{T}} \times \frac{2,754.34}{T^2} > 0. \quad E4$$

In other words, an increase in temperature will accelerate CO₂ sorption with K to a higher degree than with N. On the other hand,

$$\frac{\partial \ln K_{R1}}{\partial T} = \frac{\Delta H_{R1}}{RT^2} < 0 \quad \text{or } T \uparrow \propto q_{\text{CO}_2, R1} \downarrow \quad E5$$

$$\frac{\partial \ln K_{R3}}{\partial T} = \frac{\Delta H_{R3}}{RT^2} < 0 \quad \text{or } T \uparrow \propto q_{\text{CO}_2, R3} \downarrow \quad E6$$

and

$$\frac{\partial [K_{R1}/K_{R3}]}{\partial T} = \frac{\partial [\text{EXP}(\Delta G_{R3} - \Delta G_{R1})/RT]}{\partial T} = e^{\frac{-2,405.59}{T}} \times \frac{2,405.59}{T^2} > 0 \quad E7$$

where K_{R1} and K_{R3} represent the equilibrium constants of R1 and R3, ΔG_{R1} ($\approx \Delta G_{R1}^0 = -36.6$ kJ/mol) [15] and ΔG_{R3} ($\approx \Delta G_{R3}^0 = -50.6$ kJ/mol) [24, 25] are the Gibbs free energy changes of R1 and R3, respectively. E5, E6 and E7 indicate that the increase in temperature should negatively affect the CO₂ sorption capacities via both R1 and R3, and thus the total CO₂ capacity of SCFD-KN, as shown in the 50-80 °C range in Figure 5, although K_{R1} decreases with T relatively slower than K_{R3} does. However, the total CO₂ sorption capacity of SCFD-KN actually increases with T in the 25-50 °C range, as shown in Figure 5, which is probably due to more water condensations on the surface of the sorbent at lower temperatures. The liquid water resulting from condensation could plug the pores especially small pores of the sorbent,

increase mass transfer resistance, and thus decrease the CO₂ sorption of the sorbent.

Moisture

Enough H₂O is necessary for K based CO₂ sorption and the increase in CO₂ sorption capacity of N based sorbents, according to R1, R3 and R4. The concentrations of water in the inlet gas have significant effects on CO₂ sorption capacities, as demonstrated in Figure 6. Without the presence of H₂O, K₂CO₃ cannot react with CO₂ or R1 cannot proceed, while -NH₂ in SCFD-KN still can react with CO₂ through R4 whose ΔG_{R4}^0 and E_{R4} are -25.0 kJ/mol and 14.6 kJ/mol, respectively [22, 24]. Therefore, the sorbent still shows CO₂ sorption capacity of 0.72 mmol-CO₂/g-KN. When moisture was introduced, R1, R3 and R4 occurred simultaneously, although R1 and R3 definitely compete for H₂O. At lower temperatures, it is likely that R3 should dominate and be the main H₂O consuming reaction since R3 not only has the lower activation energy but also has the higher Gibbs free energy change, as discussed early. However, according to E4 and E7, the role R1 plays in the overall CO₂ sorption increases with temperature, and various pathways or species including (-NH₃⁺)(OH⁻), NH₃⁺, (-NH₃⁺)(-NHCOO⁻) and (-NH₃⁺)(HCO₃⁻) exist with CO₂ sorption by -NH₂ within a moisture-containing environment [8]. Therefore, the selectivity of the three overall or apparent reactions in the presence of H₂O becomes complicated but can be studied if the thermodynamic and kinetic parameters of R1, R3 and R4 are available either through experiments or by literature. The study can be used not only for predicting the effect of H₂O on

selectivity but also for optimizing the reaction conditions and thus sorption capacity.

The highest CO₂ sorption capacity, 3.02 mmol/g-KN, was achieved with $c_{H_2O,0} : c_{CO_2,0}$ mole ratio being 1.2, higher than stoichiometric value, 1. CO₂ has low solubility in H₂O and overdosing H₂O to some degree can increase the quantity of CO₂ in the quasi-liquid layer [21] between bulk gas and solid phases in the heterogeneous CO₂ sorption system, and thus increase in CO₂ sorption capacity.

Gas flow rate

The effect of gas flow rate on CO₂ sorption capacity was evaluated and the results are presented in Figure 7. Under the given conditions, CO₂ sorption capacity of the SCFD-KN sorbent increases with gas flow rate. CO₂ sorption capacities of the KN sorbent increase from 2.15 to 3.32 mmol-CO₂/g-KN as gas flow rate increases from 300 ml/min to 700 ml/min. This fact can be explained with the following relationship that Tuwati, et al [21] obtained with the sorption equation set by Yan, et al [26].

$$\frac{\partial q_{CO_2}}{\partial Q} = \frac{Qt}{k_y m} \left[\frac{c_{CO_2}}{c_{CO_2,0} - c_{CO_2}} \right]^{\frac{k_y c_{CO_2,0}}{Q}} \left[2 - \frac{k_y c_{CO_2,0}}{Q} \ln \frac{c_{CO_2}}{c_{CO_2,0} - c_{CO_2}} \right] \quad E8$$

where q_{CO_2} is CO₂ sorption capacity, Q is gas flow rate, k_y is the sorption kinetic rate constant, m is the mass of SCFD-KN, t is the sorption time, and $c_{CO_2,0}$ and c_{CO_2} are the CO₂ concentrations in inlet and outlet gases, respectively. When

$\frac{k_y c_{CO_2,0}}{Q} \ln \frac{c_{CO_2}}{c_{CO_2,0} - c_{CO_2}}$ is smaller than 2, then q_{CO_2} increases with Q , which is the case

observed with this research. The degree of CO₂ sorption capacity increase with gas

flow rate is due to the dominance of the decrease in $\left[\frac{c_{CO_2}}{c_{CO_2,0} - c_{CO_2}}\right]^{\frac{k_1 c_{CO_2,0}}{Q}}$ in the right side of E8, which results from the increase of Q in $\frac{k_1 c_{CO_2,0}}{Q}$.

Regeneration

The CO₂ sorption capacity of the regenerated SCFD-KN is important since any applicable sorbents need to perform well with multiple CO₂ sorption and desorption tests. Figure 8 demonstrates the working capacities of the sorbent over 10 CO₂ separation cycles conducted with 1 vol-% CO₂ gas mixture under the condition of sorption at 40 °C and desorption at 150 °C. The working capacities of the SCFD-KN sorbent during the cyclic CO₂ separation were kept at ~2.8 mmol-CO₂/g-KN, indicating that the sorbent is stable over multiple cycles. Its stability was also evaluated by comparing the FTIR spectra (Figure 9) of the fresh sorbent to that of the regenerated sorbent. The characteristic bands of the fresh sorbent are the same as those of the regenerated sorbent, indicating that SCFD is an advanced technology to prepare not only capable but also regenerable composite CO₂ sorbent.

CONCLUSION

A kind of alternative KN-based CO₂ sorbent, dried with supercritical method, has been synthesized and evaluated for its performance on separation of CO₂ from flue gas. Sorption tests were carried out under different conditions including those temperatures, H₂O concentration and flow rates rarely tested on lab-scale by other

researchers but important to the applications of any CO₂ sorbents. The CO₂ sorption capacities of SCFD-KN sorbent achieved with 1 vol-% gas mixture is higher than CD-KN sorbent due to the difference in densities and structures. Moreover, KN sorbent is regenerable based on the good repeatability of CO₂ sorption capacities obtained during multi-cycle CO₂ sorption-desorption tests. The equipment requirements for separation of CO₂ with KN sorbent should be less challenging than those for other CO₂ separation technologies because KN sorbent can be regenerated at 150°C, lower than those of conventional K₂CO₃-based sorbent. Correspondingly, the capital energy needs for the CO₂ separation technology should be rather low. The operation costs of KN-based CO₂ separation process can be considerably reduced due to its high CO₂ sorption capacity, fast CO₂ sorption and desorption kinetics as well as the good regenerative ability of the sorbent.

There is still room for the technology to be further improved. For example, the BET surface area and pore volume of KN sorbent could be improved for enhancement of CO₂ sorption capacity because the KN sorbent used in this research has lower BET surface area and pore volume than the majority of other organic sorbents, although its CO₂ sorption capacity is higher than theirs. Finally but importantly, all the parameters in the proposed kinetic model need to be established using thermodynamic and kinetic theories as well as experiments for optimization of the CO₂ separation technology and eventually other Amine based CO₂ separation processes. The CO₂ conversion ratio of Amine is lower, and it's significant to find Amine-loaded organic chemicals with better CO₂ sorption performance.

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NOMENCLATURE

k_{R1} , k_{-R1} , k_{R3} , k_{-R3} the corresponding rate constants of forward and reverse processes of R1 and R3, min^{-1}

A_{R1} , A_{R3} the corresponding factors of Arrhenius forms of the forward reactions of R1 and R3, min^{-1}

$c_{K_2CO_3}$, c_{CO_2} , c_{H_2O} , c_{KHCO_3} , c_{-NH_2} , $c_{[-NH_3]^+[-HCO_3]^-}$ the concentrations of K_2CO_3 , $KHCO_3$, CO_2 , H_2O , $-NH_2$, and $(-NH_3^+)(-HCO_3^-)$, mol/cm^3
 $c_{CO_2,0}$, the CO_2 concentrations in inlet gas, mol/cm^3

t the sorption time, min

$n_{K_2CO_3,R1}$, $n_{CO_2,R1}$, $n_{H_2O,R1}$, $n_{KHCO_3,-R1}$, $n_{-NH_2,R3}$, $n_{CO_2,R3}$, $n_{H_2O,R3}$, $n_{[-NH_3]^+[-HCO_3]^-,-R3}$ the reaction orders with respect to K_2CO_3 , CO_2 , H_2O , $KHCO_3$, $-NH_2$, CO_2 , H_2O and $(-NH_3^+)(-HCO_3^-)$ in the two reversible R1 and R3.

K_{R1} , K_{R3} the equilibrium constants of R1 and R3,

ΔG_{R1} and ΔG_{R3} the Gibbs free energy changes of R1 and R3, kJ/mol

q_{CO_2} CO_2 sorption capacity, mmolCO_2/g sorbent

Q gas flow rate, mL/min

349 m the mass of SCFD-KN, g

350 **Abbreviations**

351 APTES 3-aminopropyltriethoxysilane

352 TEOS tetraethylorthosilicate

353 SCFD supercritical fluid drying approach

354 CD conventional drying approach

355 KN the composite sorbent

356 SCFD-KN the composite sorbents dried with supercritical fluid drying method

357 SCFD-N a amine-silica sorbent dried with supercritical fluid drying method

358 CD-KN the composite sorbents dried with conventional approach

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360 **REFERENCE**

361 [1] S. Bakker, H. Coninck, H. Groenenberg, Progress on including CCS projects in
362 the CDM: Insights on increased awareness, market potential and baseline
363 methodologies, Int. J. Green Gas Cont. 4 (2010) 321–326.

364 [2] H. Coninck, J. Stephens, B. Metz, Global learning on carbon capture and storage:
365 A call for strong international cooperation on CCS demonstration, Energy Policy.
366 37 (2009) 2161–2165.

367 [3] L.C. Skinner, S. Fallon, C. Waelbroeck, E. Michel, S. Barker, Ventilation of the
368 deep southern ocean and deglacial CO₂ rise, Science. 328 (2010) 1147-1151.

- [4] W.M. Budzianowski, Modelling of CO₂ content in the atmosphere until 2300: influence of energy intensity of gross domestic product and carbon intensity of energy, *Int. J. Global Warming*. 5 (2013) 1-17.
- [5] A. Brunetti, F. Scura, G. Barbieri, Membrane technologies for CO₂ separation, *Journal of Membrane Sci.* 359 (2010) 115-125.
- [6] B.P. Mandal, A.K. Biswas, S.S. Bandyopadhyay, Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine, *Chem. Eng. Sci.* 58 (2003) 4137-4144.
- [7] Y. Liang, D.P. Harrison, R.P. Gupta, Carbon dioxide capture using dry sodium-based sorbents, *Energy Fuel*. 18 (2004) 569-575.
- [8] L. He, M. Fan, B. Dutcher, Dynamic separation of ultradilute CO₂ with a nanoporous amine-based sorbent, *Chem. Eng. J.* 189-199 (2012) 13-23.
- [9] O. Al-Azzawi, C.M. Hofmann, G.A. Baker, S.N. Baker. Nanosilica-supported polyethoxyamines as low-cost, reversible carbon dioxide sorbents, *J. Colloid. Interf. Sci.* 385 (2012) 154-159.
- [10] A. Aboudheir, P. Tontiwachwuthikul, A. Chakma, Kinetics of the reactive absorption of carbon dioxide in high CO₂-loaded, concentrated aqueous monoethanolamine solutions, *Chem. Eng. Sci.* 58 (2003) 5195-5210.
- [11] S. Choi, J.H. Drese, P. Eisenberger, Application of Amine-Tethered Solid Sorbents for Direct CO₂ Capture from the Ambient Air, *Environ Sci Technol.* 45 (2011) 2420-2427.
- [12] J. Wang, H. Chen, Carbon dioxide capture using polyethylenimine-loaded mesoporous carbons, *J Environ Sci.* 25 (2013) 124-132.

- [13]H. Yang, Z. Xu, M. Fan, Progress in carbon dioxide separation and capture: A review, *J Environ Sci.* 20 (2008) 14–27.
- [14]C. Gouedard, D. Picq, F. Launay, P.L. Carrette, Amine degradation in CO₂ capture. I. A review, *Int. J. Green Gas Cont.*10 (2012) 244–270.
- [15]B. Zhang, M. Fan, A. Bland, CO₂ separation by a new solid K-Fe sorbent, *Energy Fuel.* 25 (2011) 1919–1925.
- [16]IR Absorptions for Representative Functional Groups.
<http://www.chemistry.ccsu.edu/glagovich/teaching/316/ir/table.html>.
- [17]A. Chowdhury, J. Bould, Nano-powders of Na_{0.5}K_{0.5}NbO₃ made by a sol–gel method, *J Nanopart Res.* 12 (2010) 209–215.
- [18]B. Dutcher, M. Fan, Use of Nanoporous FeOOH as a catalytic support for NaHCO₃ decomposition aimed at reduction of energy requirement of Na₂CO₃/NaHCO₃ based CO₂ separation technology, *J. Phys. Chem. C.* 115 (2011) 15532–15544.
- [19]L.Ć. Ivana, K.Ć. Jugoslav, Biodiesel synthesis using K₂CO₃/Al–O–Si aerogel catalysts, *J. Serb. Chem. Soc.* 75 (2010) 789–801.
- [20]L. Dei, P. Baglioni, Aging effects on ammonium carbonate/acetone solutions and cleaning of Works of Art, *Stud Conserv.* 41(1996) 9–18.
- [21]A. Tuwati, M. Fan, A.G. Russell, J. Wang, H. Dacosta, New CO₂ sorbent synthesized with nanoporous TiO(OH)₂ and K₂CO₃, *Energy Fuel.* 27(2013) 7628–7636.
- [22]J.M. Plaza, D.V. Wagener, G.T. Rochelle, Modeling CO₂ capture with aqueous

monoethanolamine, *Int. J. Green Gas Cont.* 4 (2010) 161–166.

[23] S. Shen, X. Feng, R. Zhao, U.K. Ghosh, A. Chen, Kinetic study of carbon dioxide absorption with aqueous potassium carbonate promoted by arginine, *Chem. Eng. J.* 222 (2013) 478–487.

[24] H. Xie, Y. Zhou, Y. Zhang, J.K. Johnson, Reaction Mechanism of monoethanolamine with CO₂ in aqueous solution from molecular modeling, *J. Phys. Chem. A* 114 (2010) 11844–11852.

[25] Y. Liu, L. Zhang, S. Watanasiri, Representing vapor-liquid equilibrium for an aqueous MEA-CO₂ system using the electrolyte nonrandom-two-liquid model, *Ind. Eng. Chem. Res.* 38 (1999) 2080–2090.

[26] G. Yan, T. Viraraghavan, M. Chen, A new model for heavy metal removal in a biosorption column, *Adsorpt. Sci. Technol.* 19 (2001) 25–43.

Figure list

Figure 1 FT-IR spectra of SCFD-N, K₂CO₃ and two SCFD-KNs.

Figure 2 SEM images of typical CD-KN and SCFD-KN samples (a: CD-KN; b: SCFD-KN).

Figure 3 The typical CO₂ sorption-desorption profiles of two KN sorbents prepared with conventional and SCFD methods [Sorption (Gas composition: CO₂-1.0 vol-%; H₂O-1.0 vol-%); Gas flow rate: 0.3 L/min; Temperature: 40 °C), Desorption (N₂ flow rate: 0.3 L/min; temperature: 150 °C)].

Figure 4 Effect of K:N mole ratios on the CO₂ sorption performances of SCFD-KNs (Gas flow rate: 0.5 L/min; CO₂ concentration: 1.0 vol-%; H₂O concentration: 1.0 vol-%; Temperature: 40 °C).

Figure 5 Effect of temperature on the CO₂ sorption performance of a SCFD-KN (Gas flow rate: 0.5 L/min; CO₂ concentration: 1.0 vol-%; H₂O concentration: 1.0 vol-%).

Figure 6 Effect of H₂O concentration on the CO₂ sorption performance of a SCFD-KN (Gas flow rate: 0.5 L/min; CO₂ concentration: 1.0 vol-%; Temperature: 40 °C).

Figure 7 Effect of gas flow rate on the CO₂ sorption performance of a SCFD-KN (CO₂ concentration: 1.0 vol-%; H₂O concentration: 1.0 vol-%; Temperature: 40 °C).

Figure 8 Multi sorption-desorption performance of a SCDF-KN sorbent [Sorption (Gas composition: CO₂-1.0 vol-%; H₂O- 1.0 vol-%); Gas flow rate: 0.5 L/min; Temperature: 40 °C), Desorption (N₂ flow rate: 0.5 L/min; Temperature: 150 °C)].

Figure 9 FT-IR spectra of a SCFD-KN sorbent before and after 10 sorption-desorption cycles [Sorption (Gas composition: CO₂-1.0 vol-%; H₂O-1.0 vol-%); Gas flow rate: 0.5 L/min; Temperature: 40 °C), Desorption (N₂ flow rate: 0.5 L/min; temperature: 150 °C)].

Figure 1 FTIR spectra of SCFD-N, K_2CO_3 and two SCFD-KNs.

(a)

(b)

Figure 2 SEM images of typical CD-KN and SCFD-KN samples (a: CD-KN; b: SCFD-KN).

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Table 1 BET results for different kinds of NK sorbents

Sample		Surface area	Pore volume	Pore size
Mole ratio of K:N	Drying method	(m ² /g)	(cm ³ /g)	(nm)
2:3	SCFD	110.224	0.254	2.075
4:6	SCFD	94.347	0.216	2.441
6:9	SCFD	88.784	0.201	2.594
6:12	SCFD	64.745	0.154	3.538
8:12	SCFD	46.214	0.112	4.879
10:15	SCFD	21.874	0.072	7.758