Removal of Carbon Dioxide from Flue Gas by Ammonia Carbonation in the Gas Phase

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The increasing anthropogenic CO_2 emissions and possible global warming have challenged the United States and other countries to find new and better ways to meet the world's increasing needs for energy while, at the same time, reducing greenhouse gas emissions. This study explores the possibility of using ammonium bicarbonate (NH_4HCO_3) formation by ammonia carbonation in the gas phase to achieve reduction of CO_2 emissions from industrial flue gas. Experimental results obtained in this study demonstrate that removal of flue-gas CO_2 can be achieved via formation of solid NH_4HCO_3 through ammonia carbonation in the gas phase. Removal of CO_2 is quantified by monitoring CO_2 concentrations at the entrance and exit of the reactor column. The products of ammonia carbonation were identified by solid-state nuclear magnetic resonance analysis. For the experimental conditions employed in this study, current results show up to 50% removal of CO_2 from the flue gas. Higher efficiencies are likely achievable by optimizing the operating conditions and geometry of the reactor.

Introduction

Fossil fuels—coal, oil, and natural gas—have long been a prime "engine" of industrialized societies. They supply abundant energy at low cost. At the same time, most anthropogenic emissions are related to the use of these fuels. At present, 22 gigatons (Gt) of CO_2 per year (equivalent to 6 Gt C/year) is emitted as a result of the use of fossil fuels.[1] Coal is the fuel most widely used for the generation of electricity worldwide because it is readily available, easily transported, and relatively inexpensive. Today, 60% of all electricity in the United States is generated from coal and natural gas, while oil-derived products dominate transportation fuels. Worldwide, coal-fired power plants alone result in 1.8 of the 6 Gt C/year of CO_2 emissions, while the rest (4.2 Gt C/year) is from the use of fossil fuels in transportation, industry, and private homes. The increasing anthropogenic CO_2 emissions and possible global warming (thus climate change) have challenged the United States and other countries to find new and better ways to meet the world's increasing needs for energy while reducing greenhouse gas emissions.[2]

A new technology concept that has been developed recently in our laboratory[3,4] can potentially remove industrial greenhouse gas emissions and, at the same time, benefit both agriculture and the economy. This technology concept utilizes an innovative chemical process to convert CO_2, NO_x, and SO_x emissions into valuable fertilizers (mainly, NH_4HCO_3) that can potentially enhance sequestration of CO_2 into soil and subsoil earth layers, reduce NO_3^- contamination of groundwater, and stimulate photosynthetic fixation of CO_2 from the atmosphere. This invention integrates pollutant-removal and fertilizer-production reactions with coal-fired power plants and other energy-producing operations, resulting in a clean energy system that is in harmony with the earth's ecosystem.[5] Thus, this technology could contribute significantly to global CO_2 sequestration and clean air. Because of its potentially high efficiency and carbon credit, in addition to the benefit of clean air and stimulation of photosynthetic fixation of CO_2 from the atmosphere, this technology may lead to the removal of up to 300 million tons of CO_2 per year worldwide (equivalent to about 5% of the world's CO_2 emissions from coal-fired power plants). Instead of being released into the atmosphere from smokestacks, this amount of CO_2 will then be placed into soil and/or biomass.[6]

Real-world flue gas commonly contains approximately 15% CO_2 and 80% N_2, plus residual O_2, H_2O, and ppm levels of NO_x and SO_x. One of the key issues that needs to be investigated is whether it is feasible to reduce CO_2 emissions from the flue gas by using the following ammonia carbonation reaction to produce ammonium bicarbonate (NH_4HCO_3):

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$$CO_2 + NH_3 + H_2O \rightarrow NH_4HCO_3\downarrow$$
$$\Delta_r G^\circ = -18.05 \text{ kJ/mol} \quad (1)$$

$$\Delta_r H^\circ = -126.5 \text{ kJ/mol}$$

Calculations using published thermodynamic data[7,8] showed that the standard free-energy change ($\Delta_r G^\circ$) is −18.05 kJ/mol, which indicates that this reaction is thermodynamically favored. The thermodynamic equilibrium constant (K) for the reaction is 1459. Consequently, this reaction could potentially serve as an effective scrubbing process to remove CO_2 from the flue gas and produce a valuable product (NH_4HCO_3). Independent preliminary research on the removal of CO_2 by ammonia carbonation in aqueous ammonia solution conducted by Bai et al. has also demonstrated the validity and potential of this concept.[9] Perhaps the strongest support for this technology is the unique Chinese ammonium bicarbonate (NH_4HCO_3) fertilizer production process that was invented by Dr. Dapong He during the 1950s and was developed into full manufacturing scale during the 1960s in China.[10,11] This process achieves removal of CO_2 from coal-steam-reformed gas by formation of NH_4HCO_3 through the ammonia carbonation reaction (eq 1) to yield pure H_2 and N_2 for NH_3 synthesis. Currently, China has about 800 factories that produce 50 million tons of NH_4HCO_3 per year by using this approach. In this process, ammonia carbonation is achieved by bubbling a CO_2-containing coal-steam-reformed gas through an aqueous ammonia solution. Use of this aqueous bubbling process to remove flue-gas CO_2 in a coal-fired power plant would require a relatively large-volume scrubber (probably larger than a smokestack) and would be associated with a high capital cost, which at present may not be acceptable to the power industry. A successful carbon-management technology must be highly efficient and capable of cleaning large volumes of flue gas at a low cost. The U.S. DOE Carbon Sequestration Program requires that the avoided net costs for carbon sequestration be less than $10/ton. Therefore, the possibility of using ammonia carbonation directly in the gas phase is explored in this study, with the objective of achieving removal (or reduction) of flue-gas CO_2 emissions. Given that the chemistry of ammonia carbonation is known, the main contribution of the present study is the demonstration that removal of flue-gas CO_2 can be achieved by formation of solid NH_4HCO_3 through ammonia carbonation in the gas phase.

Materials and Methods

A schematic diagram of the test flow-reactor system employed to study the reaction of NH_3 and CO_2 in humid conditions is shown in Figure 1. The reaction among NH_3, CO_2,

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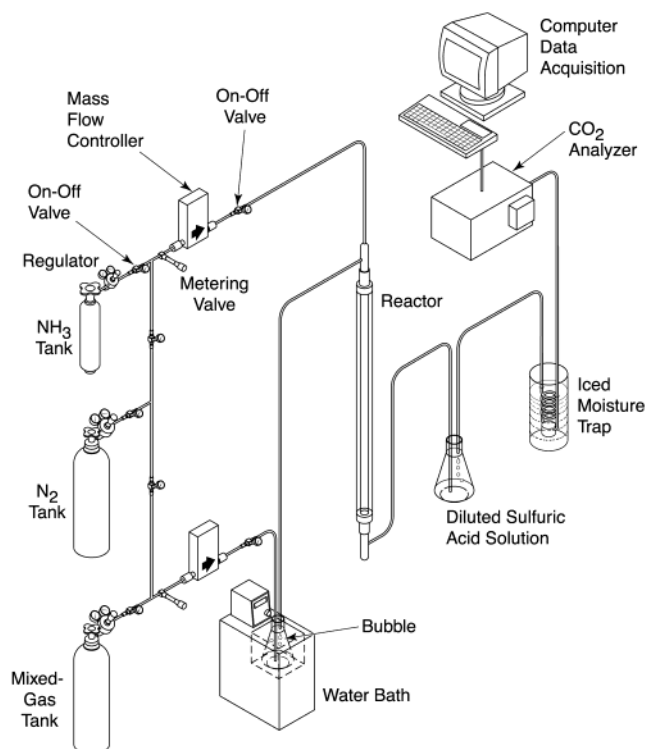
Figure 1. Schematic diagram of a test flow-reactor system for removal of CO_2 with NH_3 carbonation in the gas phase.

and water vapor was continuously performed with constant gas flows at ambient pressure and temperature in a glass tube reactor with inside diameter of 63 mm and volume of 555 mL. A compressed gas containing 15 vol % CO_2 in N_2 (primary standard, supplied by Air Liquid) was taken as a synthetic flue gas. The synthetic flue gas was continuously fed into the reactor through a side port at the top of the reactor with a controlled constant flow rate in the range of 167 to 670 mL/min while the tail gas flowing out of the reactor through its bottom port. To mimic the moisture condition of a real-world flue gas, which commonly contains a nearly saturated amount of water vapor, the synthetic flue gas was humidified by bubbling it through a water tank kept at 40 °C in an isothermal water bath (model RMS, Lauda) before it flowed into the reactor. The concentration of CO_2 in the tail gas that exited from the bottom of the reactor was monitored in-line with a digital gas analyzer (model 866, Honeywell) and recorded by DATAQ instruments. Prior to the detection of CO_2 concentration, the tail gas first went through a dilute aqueous sulfuric acid solution (1 N) for the adsorption of residual NH_3 and through an ice bath for the condensation of moisture. The compressed gas containing 15 vol % of CO_2 in N_2 (primary standard, supplied by Air Liquid) and the pure N_2 (ultrahigh purity, supplied by Air Liquid) were used to calibrate the CO_2 detector prior to each experiment, using the same procedure as that used during the experiment. The NH_3 gas was generated by evaporation from anhydrous liquid NH_3 (purity ≥99.95%) that was purchased from Sigma-Aldrich. The flow rates of NH_3 gas and flue gas were controlled by calibrated mass flow controllers (MKS Instruments, Inc.). When the initial air in the reactor was completely removed by the constant flow of the humid flue gas for more than 15 min and when the concentration of CO_2 in the outlet gas reached a steady value, ammonia gas was then introduced through a central port located at the top of the glass tube reactor. Thus, all reactants were introduced from the top of the reactor.

The yield of the process reactions (CO_2 removal efficiency) can be calculated by measuring the change of the CO_2 concentration in the tail gas that exited from the bottom of the reactor as monitored in-line with a digital gas analyzer

(model 866, Honeywell) and recorded by DATAQ instruments. The removal efficiency (E) of CO_2 (or CO_2 conversion) was determined by the CO_2 gas concentrations (volumetric percentage) in the inlet (C_i) and outlet (C_o), using the following relationship:

$$E = (C_i - C_o)/[C_i(1 - C_o)] \tag{2}$$

Although the experiments were performed at room temperature (23 °C), the actual temperature at the reaction region was increased somewhat because the reaction is exothermic. The reaction temperature was primarily dependent on the ratio of NH_3 gas flow rate to that of the flue gas. At the highest ratio of NH_3 to flue-gas flow rate used, which was 0.12, the reaction temperature was found to increase to 30 °C. The temperature was measured with a Keithley model 871 digital thermometer. The flue gas bubbling through the water tank at 40 °C deposited condensate in the tube between the water column and the reactor because of the temperature difference, and the water condensate returned to the water tank. The system was designed to ensure that no water droplets were carried into the reactor by the flue-gas humidifying system. The humidity at the inlet gas was dependent upon the room temperature but not significantly dependent on the gas flow rate. The room temperature in our experiment varied over a narrow range of 22.5−24.0 °C. The relative humidity values in the inlet port of the reactor were measured with an Alnor APM 360 relative humidity sensor. At dry flue-gas flow rates of 167, 335, and 670 mL/min, relative humidity values were measured to be 94.1, 97.3, and 97.4%, respectively. Hence, the water partial pressure was believed to be near the saturation vapor pressure, which is 2808 Pa at the room temperature (23 °C).[12] The effect of water vapor concentration on the CO_2 removal efficiency was not investigated in this study. The effect of the solid surface area inside the reactor was studied through the comparison of CO_2 removal efficiencies for two cases: an empty reactor tube and one filled with glass wool.

The solid product adhering to the inside wall of the reactor was harvested and analyzed using nuclear magnetic resonance (NMR) to confirm its identity. The solid product mixture collected in the experiment was directly analyzed by packing a powdered sample in a magic-angle spinning (MAS) rotor and acquiring the ^1H-^{13}C cross-polarization/MAS (CP/MAS) ^{13}C NMR spectrum. Solid-state ^{13}C NMR spectra were recorded on a CMX Infinity spectrometer, operating at 2.42 T, using standard ^1H-^{13}C CP/MAS techniques[13] and the following parameters: ^1H, 102.959 MHz; ^{13}C, 25.891 MHz; ^1H rf amplitude, 81 kHz (3.1 μs 90 °C pulse) held constant for ^1H excitation, cross polarization, and dipolar decoupling; 2.5-ms cross polarization contact time; 1-s pulse delay; MAS = 5030 ± 2 Hz. The Hartmann−Hahn cross polarization match condition was optimized at the first upper sideband position by varying the ^{13}C rf field amplitude. Chemical shifts are reported with respect to tetramethylsilane (TMS) ($\delta = 0$ ppm) using hexamethylbenzene as the secondary standard (δ_{methyl} = 17.5 ppm).

Results and Discussion

Effect of Reaction Conditions on the CO_2 Removal Efficiency. Figures 2A and 2B show CO_2 removal efficiency curves as a function of the reaction time for various ratios of NH_3 flow rate to the flue-gas flow rate (ranging from 0.03 to 0.12). The CO_2 removal efficiency was sharply increased as soon as NH_3 was introduced into the reactor. The initial slope of curves (within a few minutes) was dependent on a number of
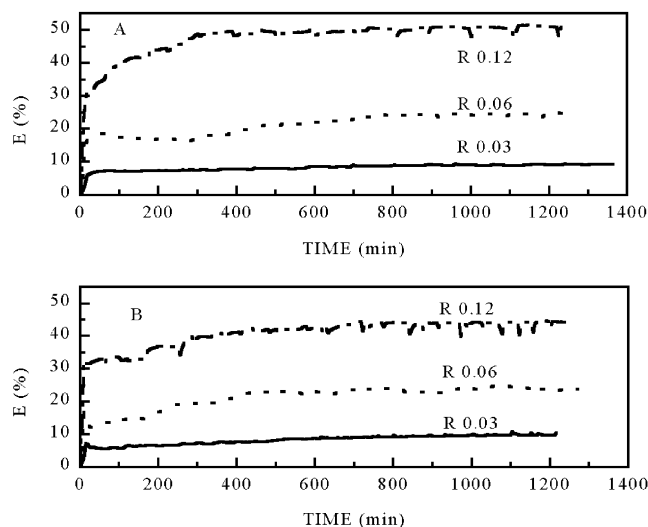
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Figure 2. Effect of the ratio (R) of NH_3 to flue-gas flow rate on CO_2 removal efficiency. (A) Flue-gas flow rate = 167 mL/min; (B) flue-gas flow rate = 335 mL/min.
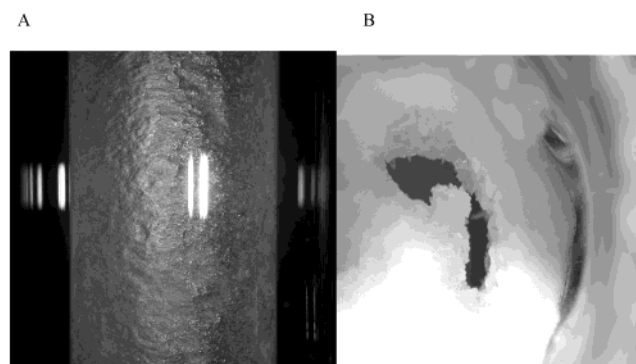

Figure 3. Photographs of solid product produced by ammonia carbonation in the gas phase. (A) Solid on the inside wall of the reactor; (B) solid viewed along the cross section of the reactor.

factors including the CO_2-detector response time, the gas flow rate, and the reactor volume. Therefore, it does not necessarily reflect the intrinsic chemical kinetics or the yield of the process reactions. Only the CO_2 removal efficiency recorded after about 10 min after the introduction of the NH_3 flow reflects the process yield.

Visually, the formation of ammonium salts (solid products) appeared immediately as a fog that condensed on the inside wall of the reactor. With the reaction proceeding for a longer period of time, the CO_2 removal efficiency smoothly increased to a steady-state (plateau) value after about 10 hours (Figures 2A and 2B). This slow but smooth increase in CO_2 removal efficiency probably reflects that the absorption of CO_2 by the conversion of $NH_2CO_2NH_4$ to NH_4HCO_3 becomes faster with an increase in the amount of $NH_2CO_2NH_4$ accumulated on the inside wall of the reactor as the process continues (see more discussion on possible reactions later in the text). As shown in Figures 3A and 3B, we observed a significant amount of solid product adhered to the inside wall of the reactor during our experiments. No solid product or particles had fallen to the bottom of the reactor, which suggests that the reaction occurs on the inside wall of the reactor or that the products have binding affinity to the reactor wall.

The results in Figures 2A and 2B also indicate that
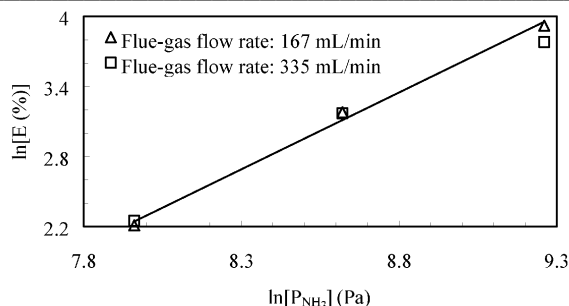
Figure 4. Logarithmic relationship between CO_2 removal efficiency (E) and NH_3 partial pressure (P_{NH_3}).

Figure 5. Effect of residence time on CO_2 removal efficiency. The ratio of NH_3 to flue gas is kept constant.

the CO_2 removal efficiency increased significantly with an increase in the ratio of NH_3 flow rate to the flue-gas flow rate. When the ratio increased from 0.03 to 0.06 and then to 0.12, the steady-state CO_2 removal efficiency increased from 9.51 to 23.7 and then to 43.6% at the flue-gas flow rate of 335 mL/min (Figure 2B), and from 9.08 to 24.0 and then to 50.4% at the flue-gas flow rate of 167 mL/min (Figure 2A). Although it is possible to further increase CO_2 removal efficiency by increasing the ratio of NH_3 flow rate to the flue-gas flow rate, our computer modeling study showed that application of this technology to remove 20−60% of the CO_2 emissions would probably yield the best return on investment for a 300- to 700-MW(e) coal-fired power plant.[14] The Kyoto Treaty requires only a 20% reduction of CO_2 emissions. A scrubbing technology that can cost-effectively remove CO_2 emissions within a practical dynamic range of 20−60% would be quite adequate to help the fossil energy industries meet the foreseeable requirement for reduction of greenhouse-gas emissions when the Kyoto Treaty is finally ratified.

Furthermore, as shown in Figure 4, a linear relationship was observed when the logarithm of the steady-state CO_2 removal efficiency, reached after 10 hours of reaction, was plotted versus the logarithm of the NH_3 partial pressure (P_{NH_3}) at the inlet. This behavior can be explained by assuming the global reaction rate (r) to be described by

$$r = FC_iE = k \cdot P_{CO_2}^{\alpha} \cdot P_{H_2O}^{\beta} \cdot P_{NH_3}^{\gamma} \qquad (3)$$

where F is the flue-gas flow rate at the inlet and k is the global reaction rate constant. The partial pressure of water vapor (P_{H_2O}) at the inlet in this experiment can be treated as a constant for a constant temperature and pressure. Moreover, the partial pressure of CO_2 (P_{CO_2}) at the inlet does not significantly decrease with the increase of the ratio of NH_3 flow rate to the flue-gas flow rate from 0.03 to 0.12, and it can be also treated as a constant. Therefore, we have the following linear relationship:

$$\ln(E) = \ln(r) - \ln(FC_i) =$$
$$[A - \ln(FC_i)] + \gamma \ln(P_{NH_3}) \quad (4)$$

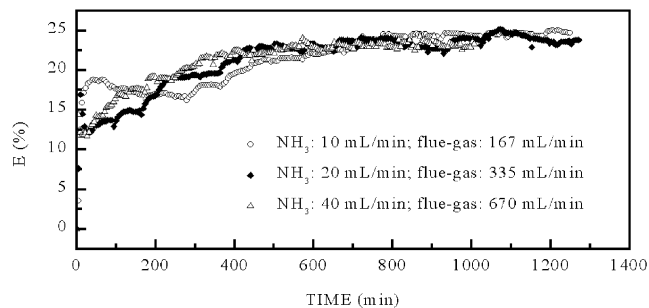where A is $\ln(kP_{CO_2}^{\alpha} \cdot P_{H_2O}^{\beta})$, which can be treated as a

constant as discussed before. For a given experiment with a fixed flue-gas flow rate (F) and a constant concentration of CO_2 at the inlet of the reactor (C_i), the term $\ln(FC_i)$ is also a constant. Therefore, the relationship between $\ln(E)$ and $\ln(P_{NH_3})$ is expected to be linear. This linear relationship between $\ln(E)$ and $\ln(P_{NH_3})$ models the experimental data well (Figure 4).

The time-dependent profile of CO_2 removal efficiency is shown in Figure 5 for three different residence times under various total flow rates (from 177 to 710 mL/min). At a fixed ratio of 0.06 for the rate of NH_3 flow to the flue-gas flow, the total flow rate was increased from 177 to 710 mL/min (not considering water vapor); thus, the residence time was decreased from 188 to 47 s. Our experimental data (Figure 5) showed that the steady-state CO_2 removal efficiency remained constant with the 4-fold decrease in the residence time. This behavior indicates that a dynamic equilibrium might be reached for the ammonia carbonation reactions in humid conditions under the given ratio of the rate of NH_3 flow to the flue-gas flow. In a comparable reaction system of NH_3−SO_2 reactions at trace water conditions reported in the literature,[15] the independence of sulfur dioxide removal efficiency on the reactor residence time has also been observed at residence times longer than 0.4 s.

Another parameter that was tested is the effect of surface area in the reactor. Because the solid product was formed on the inside wall of the reactor, it was speculated that a higher surface area in the reactor might increase the CO_2 removal efficiency. Figures 6A and 6B show the comparison curves for the CO_2 removal efficiency as a function of time for two configurations of the reactor tube: (1) vacant and (2) packed with glass wool. Figure 6 shows that the CO_2 removal efficiency was independent of the surface area in the reactor. This result suggested that the reaction of ammonia carbonation, at least the rate-determining step, occurs in the gas phase. Adsorption phenomena might be the main reason that the solid product accumulates on the inside wall of the reactor.

Analysis of Solid Product. The possible reactions among NH_3, CO_2, and H_2O were reviewed in the recent article of Bai and Yeh.[16] Among these reactions, there are two alternative mechanisms for the formation of ammonium bicarbonate from CO_2, H_2O, and NH_3.[11] In the first mechanism, dissolution of ammonia into water takes place, forming an aqueous ammonia solution, and

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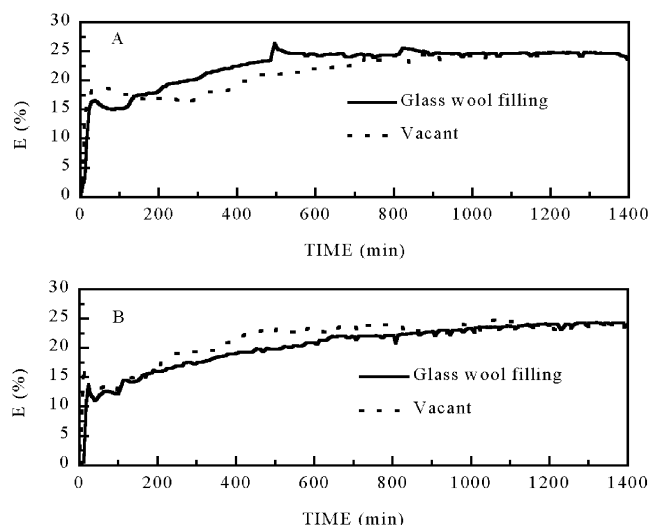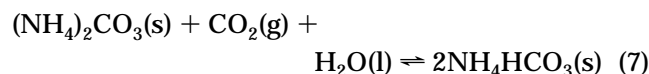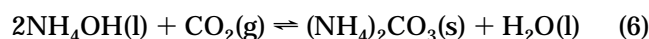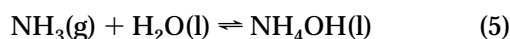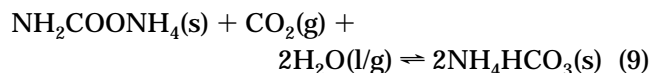(16) Bai, H. L.; Yeh, A. C. *Ind. Eng. Chem. Res.* **1997**, *36*, 2490−2493.

Figure 6. Effect of solid surface area on CO_2 removal efficiency at the ratio $R = 0.06$ of NH_3 to flue-gas flow rate. (A) Flue-gas flow rate = 167 mL/min; (B) flue-gas flow rate = 335 mL/min.

ammonium carbonate is then formed as an intermediate by the reaction of NH_3 and CO_2 in aqueous solution. The ammonium carbonate is further transformed into ammonium bicarbonate by the reaction with CO_2 and H_2O. The reaction sequence is as follows:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4OH(l) \tag{5}$$

$$2NH_4OH(l) + CO_2(g) \rightleftharpoons (NH_4)_2CO_3(s) + H_2O(l) \tag{6}$$

$$(NH_4)_2CO_3(s) + CO_2(g) + H_2O(l) \rightleftharpoons 2NH_4HCO_3(s) \tag{7}$$

In the second mechanism, ammonium carbamate is first formed by the reaction of NH_3 with CO_2 in the gas phase, which is further hydrolyzed into ammonium bicarbonate. The reaction sequence is as follows:

$$2NH_3(g) + CO_2(g) \rightarrow NH_2COONH_4(s) \tag{8}$$

$$NH_2COONH_4(s) + CO_2(g) + 2H_2O(l/g) \rightleftharpoons 2NH_4HCO_3(s) \tag{9}$$

Although three solid products are postulated for these mechanisms, only two solid products were observed in the reaction between NH_3 and CO_2 in humid conditions. These products are NH_4HCO_3 and NH_2COONH_4, as shown in Table 1. This result is consistent with the second mechanism of ammonia carbonation for production of ammonium bicarbonate.

Figure 7 shows representative solid state ^{13}C NMR spectra of (a) ammonium bicarbonate, (b) ammonium carbamate, and (c) a reactor product mixture consisting of 40 mol % ammonium bicarbonate and 60 mol % ammonium carbamate. Spectrum 7a shows the bicarbonate resonance as a sharp ($\nu_{1/2} = 26$-Hz) peak at 163.8 ppm.[17] The asymmetric doublet in spectrum 7b (163.8 ppm, 171.9 ppm, each with $\nu_{1/2} \approx 85$-Hz, and intensity ratio of 2:1) is the resonance of the carbonyl carbon of
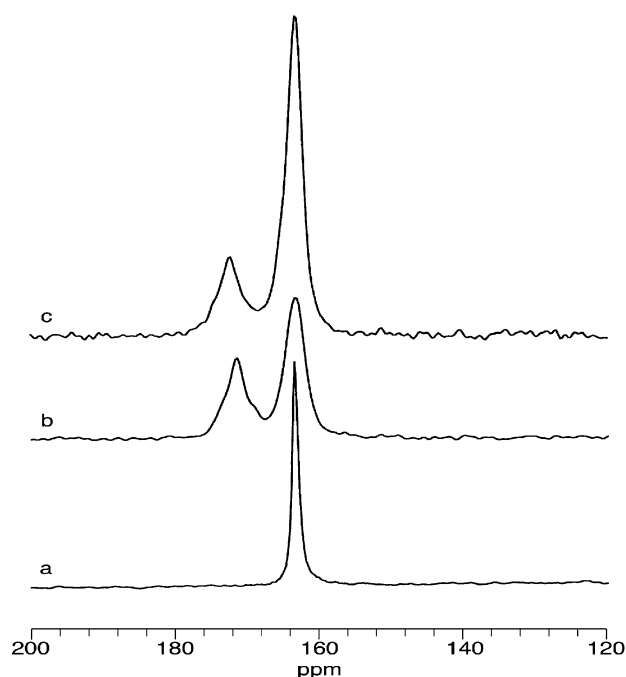
(17) The line width of this resonance is actually 6 Hz, but has been broadened by exponential apodization to remove the sync wiggle artifacts from free induction decay truncation.

Figure 7. Solid state ^{13}C NMR spectra of (a) NH_4HCO_3, (b) NH_2COONH_4, and (c) a product containing a mixture of the two.

the carbamate, which displays $^{13}C-^{14}N$ dipolar coupling to the ^{14}N quadrupole.[18] The splitting arises since the ^{14}N spin functions are not pure Zeeman states but are determined by the Zeeman-quadrupole Hamiltonian. The mixing of states produces an angular dependence of the dipolar interaction that is not averaged to zero by MAS and gives ^{14}N-bonded ^{13}C nuclei this characteristic appearance.[19] One component of the doublet happens to be accidentally degenerate with the chemical shift of the bicarbonate resonance (spectrum 7a). The spectrum of an actual mixture of the two components, shown in spectrum 7c, differs from a simple weighted sum of spectra 7a and 7b in that the line width of the pure bicarbonate resonance (spectrum 7b) is broadened in the mixture, a consequence of magnetic susceptibility broadening.[20] Nevertheless, the mole fraction of the two components is readily determined by integration of the spectrum, dividing the area at the saddle point, and assigning the area of the 171.9-ppm peak as 1/3 the total area of the carbamate component. The area balance is attributed to the bicarbonate moiety. Since each substance contains just one carbon, the area ratio is the mole ratio of the two components. The diamide urea is a possible though not an expected product under the current experimental conditions. It is not readily measurable by solid-state NMR, because of its long ^1H spin lattice relaxation time. The absence of urea in all products was demonstrated by evaporative loss of the sample from a 60 °C hot plate, which left no residue.

Table 1 lists the chemical compositions of the solid products and the steady-state CO_2 removal efficiency after 10-h reaction in the experiments. For the chemical

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Table 1. Composition of Solid Product and Steady-State CO₂ Removal Efficiency for Different Reaction Conditions

	A10M335[a]	A20M335[b]	A40M335[c]	A10M167[d]	A40M670[e]
NH_4HCO_3, mol %	100	100	40	40	65
$NH_2CO_2NH_4$, mol %	0	0	60	60	35
CO_2 removal efficiency, %	9.51	23.7	43.6	24.0	23.1

[a] A10M335 represents NH_3 flow rate of 10 mL/min and flue-gas flow rate of 335 mL/min. [b] A20M335 represents NH_3 flow rate of 20 mL/min and flue-gas flow rate of 335 mL/min. [c] A40M335 represents NH_3 flow rate of 40 mL/min and flue-gas flow rate of 335 mL/min. [d] A10M167 represents NH_3 flow rate of 10 mL/min and flue-gas flow rate of 167 mL/min. [e] A40M670 represents NH_3 flow rate of 40 mL/min and flue-gas flow rate of 670 mL/min.

compositions of the solid products, an apparent random distribution for the ratio of ammonium bicarbonate to ammonium carbamate was observed, which might be ascribed to the instability of $NH_2CO_2NH_4$ and NH_4HCO_3 in humid conditions and the time delay between production and composition analysis. The product ratio dependence on reaction conditions was not identified in this study. However, the composition of the solid product is important to the analysis of the NH_3-scrubbing CO_2 process. For the same NH_3 consumption, the CO_2 removal efficiency would be double if the final solid product is 100% NH_4HCO_3 instead of 100% NH_2CO_2-NH_4. Therefore, further studies are needed to fully develop this NH_3-scrubbing CO_2-removal technology.

Conclusions

The removal of CO_2 by NH_3 injection was studied experimentally in a synthetic flue gas. The NH_3 concentration played an important role in CO_2 removal. No effect of the resident time on the steady-state CO_2 removal efficiency was observed, which indicated that a dynamic equilibrium might be reached for the ammonia carbonation reactions under humid conditions. This reaction occurred in the gas phase, and no enhancement of CO_2 removal efficiency was observed after a solid packing was introduced into the reactor to increase surface area. The solid ammonia carbonation products could be formed quickly in the gas-phase reaction among NH_3, CO_2, and water vapor. The experimental results demonstrated that it is possible to achieve efficient removal of flue-gas CO_2 by formation of NH_4HCO_3 and $NH_2CO_2NH_4$ through ammonia carbonation in the gas phase. Further studies are needed to determine the kinetics of the reaction and properly design a reactor for optimal operation in terms of CO_2 removal efficiency and product content.

EF020120N