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Highly Efficient and Selective Formation of Hydrogencarbonate in CO_2 Absorption Process Using Piperidine and Piperazine Derivatives

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This investigation demonstrated that bicarbonate ions were selectively formed over carbamate in a CO_2 absorption process using piperidine and piperazine derivatives based on ^{13}C NMR. Piperidines with methyl or hydroxymethyl substituent at 2 position (PiP-Me and PiP-MeOH) and 2,5-dimethylpiperazine (DM-PiZ) generated the bicarbonate ions as main adducts in reaction with CO_2. The absorptions of CO_2 by those aqueous amines (PiP-Me and DM-PiZ) were faster than those of MEA (2-aminoethanol).

Recently, there has been increasing demand for green energy and environmentally related areas: specifically, post combustion CO_2 capture (PCC). In order to address this problem, many different technologies have been tried, including water-soluble amines,[1,2] using solid amines,[3] ionic liquid,[4] or porous supports,[5] cryogenic and membrane separation,[6] and biological conversion.[7] Thanks to its high capacity for CO_2 absorption at a low CO_2 partial pressure, amine-based absorption techniques have been considered as the most promising technology in PCC.[8]

In the progress of amine-based absorption technology, it has been reported that a certain type of amine,[9,10] a mixture of different types of amine,[11,12] finding the optimum absorption process conditions and controlling the stability and reactivity enhance the CO_2 absorption efficiency. However, many researchers have focused on which alternative amine makes it possible to overcome amine disadvantages, including solvent loss and high desorption energy.[13,14] Recently, we proposed that enhancing the hydrogencarbonate (bicarbonate, BC) selectivity process may solve the cumbersome problem of high desorption energy in CO_2 absorption.[15]

Thus far researchers know that CO_2 is converted into mixtures of carbamate (CB) and BC in the amine-based CO_2 absorption process. In general, CB is formed quickly, but it requires high desorption energy. Whereas carbonate is formed more slowly and it requires only low desorption energy. In other words, CB can be stably stored and BC can easily reproduce CO_2.[8] Thus, if CO_2 is converted and separated only in one form of the intermediates CB or BC, then the storage and desorption processes for CO_2 could be implemented in PCC more efficiently than the CB–BC mixture could.

The reaction mechanisms for the amine-based CO_2 capture vary depending on the structure of the amines (eqs 1–3). In primary or secondary amines, which can provide protic cations, two moles of amines absorb one mole of CO_2 to form carbamate ions (eq 1) then undergo hydrolysis to produce bicarbonate or carbonate. In tertiary amines, which are not capable of releasing H^+ ions, these amines do not generate carbamate; CO_2 is converted to bicarbonate, but slowly in the same molar ratio (eq 3).[16–19]

(1) Carbamate formation (1° and 2° amines)

$$2\ RR'NH + CO_2 \rightleftharpoons RR'NCOO^- + RR'NH_2^+ \qquad (1)$$

(2) Conversion of carbamate to bicarbonate

$$RR'NCOO^- + H_2O \rightleftharpoons HCO_3^- + RR'NH \qquad (2)$$

(3) Bicarbonate formation (3° amine)

$$R_3N + CO_2 + H_2O \rightleftharpoons HCO_3^- + R_3NH^+ \qquad (3)$$

In principle, the conversion of CB to BC as in eq 2 would depend on the structures of amines resulting in different steric or electronic effects. With this fact in mind for the selective formation of BC in the amine-based CO_2 absorption process, we carried out the CO_2 absorption process in the presence of secondary amine derivatives, as shown in Figure 1. In terms of selectivity, the primary amines are highly inclined to form carbamates. Meanwhile, tertiary amines are known to react with CO_2 too slowly to form BC ions in practical PCC applications.[20]

The experimental devices for amine-based CO_2 absorption are composed of a supplier, a reactor, and a data collector, as shown in Figure 2. In the experiment, 99.99% purity CO_2 gas

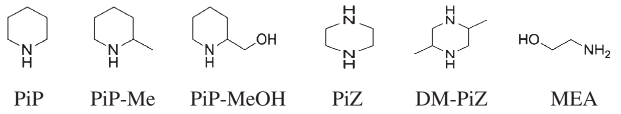


Figure 1. The structures, names, and abbreviations of amines used for CO_2 absorption.

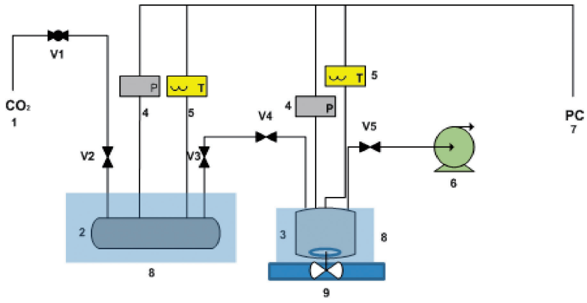
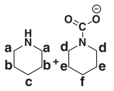
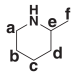
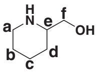
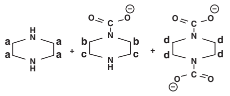
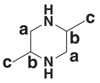


Figure 2. Experimental apparatus for CO_2 absorption: 1) CO_2 gas cylinder, 2) reservoir, 3) reactor, 4) pressure transducer, 5) thermometer, 6) vacuum pump, 7) data acquisition and analysis, 8) water bath, 9) magnetic stirrer, (V1–V5) valves.

Table 1. ^{13}C NMR data of amines before and after CO_2 absorption for 2 h

Structure	Sample	Chemical shift values/ppm							
		sp^3-Carbon						sp^2-Carbon	
		a	b	c	d	e	f	CB	BC
	PiP[a]	45.7	25.7	24.2	—	—	—	—	—
	PiP + CO_2	44.5	22.6	21.8	45.3	25.5	24.1	163 0.3	161.1
	PiP-Me[a]	45.7	24.9	24.2	33.5	51.4	21.7	—	—
	PiP-Me + CO_2	44.3	21.6	21.5	30.0	52.7	18.5	no[b]	160 0.5
	PiP-MeOH[a]	45.7	28.0	25.4	23.9	57.4	66.1	—	—
	PiP-MeOH + CO_2	44.6	24.7	21.4	22.1	58.1	62.0	no	160 0.9
	PiZ[a]	44.7	—	—	—	—	—	—	—
	PiZ + CO_2	42.6	43.5	41.5	44.2	—	—	162 0.3	160 0.5
	DM-PiZ[a]	49.6	52.0	18.5	—	—	—	—	—
	DM-PiZ + CO_2	48.9	49.2	16.6	—	—	—	no	160 0.8

[a]In neutral condition before addition of CO_2. [b]Not observed.

was used. The reactor was made of stainless steel and its volume was 49.5 cm^3.

All the experiments were conducted at room temperature. Initially, 10 g of 30 wt% (distilled water 7 g + absorbents 3 g) amine absorbents were injected into the reactor. The exception was PiZ, which was used at 8 wt% as its solubility in water was too low. Any gases remaining in the reactor were removed by opening valve V5 and using a vacuum pump. When the pretreatment had been completed, valve V5 was closed and valve V4 was opened to inject CO_2 in the supplier into the reactor. The pure CO_2 pressure was controlled to be around 1.0–1.2 bar. This process was repeated until amine absorbents did not absorb CO_2 any further. The numbers of CO_2 injections were between six and fourteen depending on the amine absorbents. The reactions were completed within about two hours.

For NMR spectroscopic analysis, a certain amount (ca. 200 µL) of reaction mixture was diluted in D_2O or $CDCl_3$ and analyzed using a 200 or 500 MHz NMR spectrometer (Bruker Ltd.) and the result is presented in Table 1. The formation of CB or BC ions were identified by the C=O peak near 160–168 ppm.[21,22] As examples, ^{13}C NMR spectra of PiP and PiP-Me are shown in Figures 3 and 4. The C=O peaks of the CB formed from reactions with CO_2 with PiP and PiZ derivatives were identified at near 163 and 162 ppm, respectively. The chemical shift (δ) values of the C=O peaks of CB were not affected by pH changes caused by different CO_2 loading, as represented by other researchers.[8] However, the chemical shift (δ) value of BC showed different values depending on the pHs of surrounding solutions.[22] As reaction time went on, the position of C=O peaks of BC in PiP and PiZ derivatives shifted toward the upfield regions. In the case of PiP-Me, it moved to 160.5 ppm from 165.5 ppm after 2 h as shown in Figure 4. The carbonate (CO_3^{2-}) was not distinguished from the bicarbonate because only one peak was formed[22] as protons were quickly exchanged between bicarbonate and carbonate.

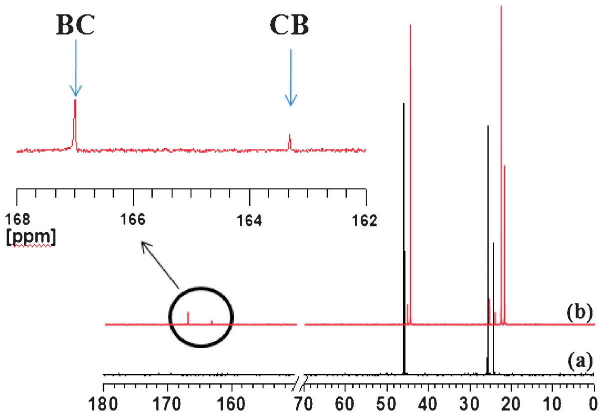


Figure 3. ^{13}C NMR data of PiP before (a) and 1 h after (b) CO_2 absorption.

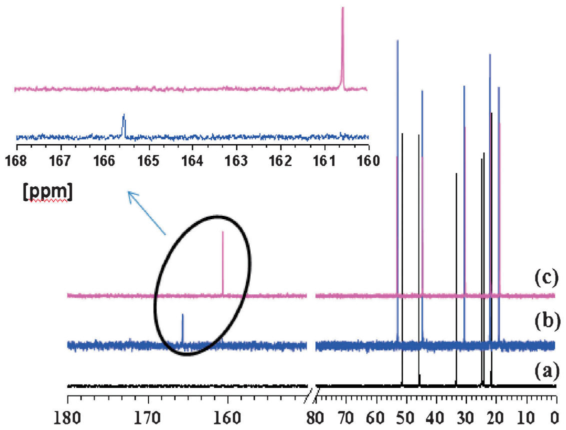


Figure 4. ^{13}C NMR data of PiP-Me before (a) and after (b, c) CO_2 absorption for 1 and 2 h, respectively.

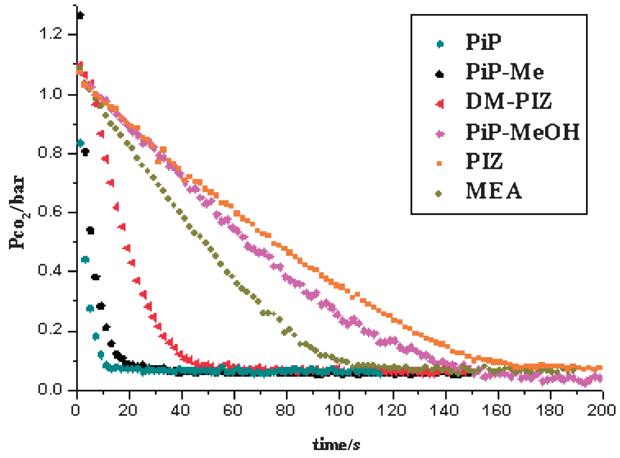


Figure 5. The absorption of 1st injected CO_2 by aqueous amine solution (30 wt% amine solutions in water were used except 8 wt% for PiZ).

In general, the secondary amines PiP and PiZ compounds in the neutral state were not distinguished from the protonated forms ($PiPH^+$ and $PiZH^+$) because protons were quickly exchanged between the amines in equilibrium. Specifically, these results were confirmed by the NMR spectroscopies of the PiP derivatives as shown in Figures 3 and 4.

In terms of selectivity of BC over CB, as summarized in Table 1, this result illustrates that piperidine and piperazine derivatives containing methyl or hydroxymethyl groups at the 2 or 5 position, PiP-Me, PiP-MeOH, and DM-PiZ, yielded BC ions only in the course of the CO_2 absorption process. On reviewing the ^{13}C NMR of PiP-Me after absorption of CO_2 (Figure 4), CB was not formed and only a BC peak existed near 160 ppm. Similarly, in the case of PiP-MeOH, only a carbonyl peak from BC ions was observed at 160.9 ppm. The NMR of PiZ after CO_2 absorption represents the CB/BC peaks of PiZ at 162.3/160.5 ppm, respectively. Meanwhile, only a BC peak of DM-PiZ appeared at 160.8 ppm. It is quite an intriguing result that piperidine and piperazine derivatives with alkyl substituent at the α carbon produced BC only, while it was also expected to form CB over BC in the early stage of CO_2 absorption process. One of the possible explanations would be that the formation of carbamate from PiP-Me and PiP-MeOH was suppressed because they were readily converted to BC due to steric effects.

In addition to the selectivity of BC, the CO_2 absorption was also investigated based on the CO_2 pressure drop in the presence of different types of secondary amines along with MEA as a reference, as shown in Figure 5. The amines, PiP, PiP-Me, and DM-PiZ, showed faster pressure drop than the standard sample MEA. This may be attributed the fact that secondary amines have higher basicity than MEA due to the inductive effect of alkyl groups. PiP-MeOH, which has hydrophilic hydroxy (OH) groups showed much slower absorption than the structurally similar amines PiP-Me or MEA. This result agrees with the previous report that hydroxyamines usually represent a lower CO_2 loading capacity than that of alkylamines.[23]

In conclusion, cyclic secondary amines, piperidine and piperazine, generally formed both carbamate and bicarbonate in the CO_2 absorption process. However, it was discovered that when their position numbers 2 or 5 had been substituted by alkyl or hydroxy alkyl groups, only bicarbonate was formed. Initial absorption rates of piperidine (PiP and PiP-Me) and piperazine (DM-PiZ) derivatives were faster than those of MEA, which is currently used in the industrial market for PCC.

Based on these results, we conclude that it will be possible to selectively collect bicarbonate only in the process of amine-based CO_2 absorption and therefore, this process can be used to improve the PCC process to be more efficient in terms of desorption energy.

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