

Reversible Capture of CO₂ by Cucurbit[7]uril Absorbent

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Abstract— Traditional amine absorbents for CO₂ are oftentimes corrosive to equipment and degrade through oxidation, thus severely restricting the wide application in CO₂ capture. Herein, a supramolecular approach to CO₂ capture by cucurbit[7]uril (CB[7]) complex was developed. NH₂(CH₂)₆NH₂⋅CB[7] complex can convert CO₂ to bicarbonate product. Furthermore, the CB[7] complex can be reused to absorb CO₂ over 5 times in solid state, thereby providing a green absorbent to CO₂ with regard to high stability, non-corrosiveness and convenient transportation.

Keywords- Carbon dioxide; Capture; Cucurbituril; Absorbent

I. INTRODUCTION

CO₂ is one of the major greenhouse gases, and huge amounts of CO₂ are released into the air upon the burning of fuels, such as oil, coal, wood and natural gas. As a result, CO₂ is accumulating faster in the atmosphere than the earth's natural processes, i.e., plants and aqueous resources, can absorb. On the other hand, CO₂ can be used as an important carbon resource. Therefore CO₂ fixation becomes a very attractive subject not only due to increasing environmental concerns, but also in view of carbon resource utilization [1]. It is well-known that CO₂ reacts with amines rapidly at room temperature and can be released easily by gentle heating (60-110 °C) or simply by addition of HCl or TFA [2]. This reversible conversion leads to controllable capture and release of CO₂ from the air. However most of the amines are corrosive to equipment and degrade through oxidation, thus severely restricting their wide application in CO₂ capture. To solve the problems, amine-modified solid sorbents supported on silica gels [3], molecular sieves and polymers [4] have been designed and synthesized.

Cucurbit[n]urils (CB[n], n = 5-10) are cyclic oligomers of glycoluril with an interior hydrophobic cavity and polar carbonyl groups surrounding the two identical portals [5]. They can accommodate cationic and neutral guests through ion-dipole interactions, hydrophobic effect or hydrogen bonds [6,7]. Mock firstly reported that 1,3-dipolar cycloaddition reaction could be accelerated by a factor of 5.5×10⁴ under the influence of CB[6] [8]. Afterwards, applications of CB[n] as catalyst were investigated in a variety of reactions, such as hydrolysis reaction, solvolytic reaction, desilylation reaction, thiol-disulfide interchange reaction, oxidation reaction, and photoreactions [9]. So far,

application of CB to convert CO₂ has been rarely investigated [10].

Based on the unique characteristics of recognition and assembly for supramolecular macrocyclic host structures, amine-modified calixarene [11] and crown ethers [12] have been designed for construction of novel nanostructures and materials. In this work, without resort to the chemical modification step of amino group, a supramolecular approach to CO₂ capture catalyzed by CB[7] was developed.

II. EXPERIMENTAL

A. Materials and Apparatus

¹H and ¹³C NMR spectra were recorded on Bruker DRX-400 spectrometer for ¹H at 400 MHz and for ¹³C at 100 MHz. The highly pure CO₂ (99.999%) was obtained from local supplier. CB[7] was synthesized using a published procedure [13] and characterized by NMR prior to use. NH₂(CH₂)₆NH₂⋅CB[7] complex was readily prepared by mixing solid CB[7] (100 mg) with excess of 1,6-hexanediamine (2.000 g) at 50 °C for 3.5 h. After filtration, the uncomplexed amine was washed out thoroughly with methanol. The white powder was dried under vacuum at 70 °C for 3 h (49% yield based on CB[7]).

B. CO₂ Reaction

NH₂(CH₂)₆NH₂ or NH₂(CH₂)₆NH₂⋅CB[7] complex (0.004-0.05 M) was dissolved in D₂O in a 5 mm NMR tube. CO₂ was then bubbled through the solution at 25 °C with a flow rate of 10 mL/min as regulated by flow meter. The CO₂ reactions were monitored by ¹H and ¹³C NMR spectra.

C. CO₂ TPD experiment of NH₂(CH₂)₆NH₂⋅CB[7] Complex

The multi-cycle temperature-programmed desorption (TPD) of CO₂ was conducted in an AutoChem 2910 unit (Micromeritics) equipped with a thermal conductivity detector (TCD). The sample cell was loaded with ca. 60 mg of NH₂(CH₂)₆NH₂⋅CB[7] complex. After it was heated in flowing helium to 50°C, a CO₂ flow was introduced to the sample cell for CO₂ adsorption for 1 h. Then the sample was swept using flowing helium to remove the weakly adsorbed CO₂. Afterwards the TPD experiment was carried out from 50 to 150 °C with a heating ramp of 5 °C/min, then kept at 150 °C for 15 min. After temperature was cooled to 50 °C, the next run for CO₂ adsorption and TPD experiments were performed following the same procedure.

III. RESULTS AND DISCUSSION

The $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{CB}[7]$ complex was synthesized and characterized by ^1H NMR (Figure 1), wherein 1:1 host-guest ratio could be derived from the integration and the resonance signals assigned to amine moving up field indicate their positioning within the cavity of CB[7]. For reaction of $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{CB}[7]$ complex with CO_2 in aqueous solution, the new resonance signal on ^{13}C NMR spectrum at δ 159.8 ppm was assigned to bicarbonate as the only product of CO_2 fixation, while carbamate product was not detected (Figure 2b).

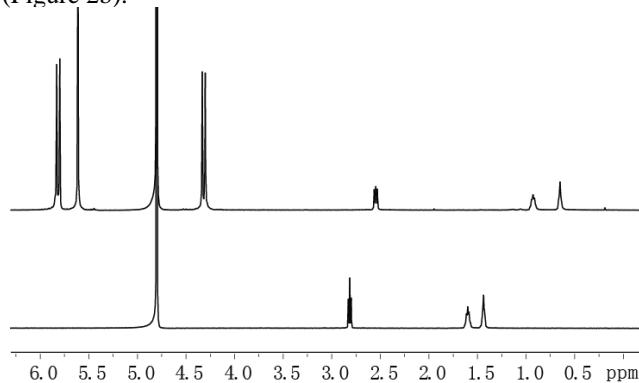


Figure 1. ^1H NMR spectra of $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ (bottom) and $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{CB}[7]$ (top) in D_2O .

The bicarbonate product of $(\text{NH}_3^+(\text{CH}_2)_6\text{NH}_3^+\text{CB}[7])\cdot 2\text{HCO}_3^-$ remained stable in solution even after heating at 90°C for 10 h. Through rotary evaporation to remove water, $(\text{NH}_3^+(\text{CH}_2)_6\text{NH}_3^+\text{CB}[7])\cdot 2\text{HCO}_3^-$ powder was obtained, whereas CO_2 could be released by heating at 150°C for 3 h (Figure 2).

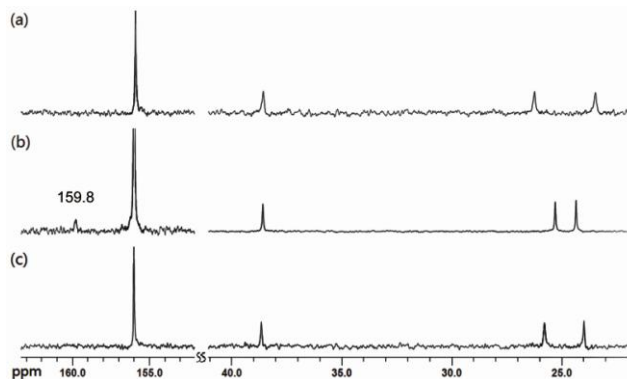


Figure 2. ^{13}C NMR spectra of (a) $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{CB}[7]$, (b) after bubbling CO_2 into $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{CB}[7]$, (c) after heating $(\text{NH}_3^+(\text{CH}_2)_6\text{NH}_3^+\text{CB}[7])\cdot 2\text{HCO}_3^-$ powder at 150°C for 3 h (D_2O).

Furthermore, in order for the practical application of CB[7] complex as CO_2 absorbent, multi-cycle temperature-programmed desorption (TPD) of CO_2 on $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{CB}[7]$ in the solid state has been

undertaken. As illustrated in Figure 3, the reusability of CB[7] complex for CO_2 capture have been demonstrated over 5 cycles, exhibiting high reversibility and stability of CB[7] complex to absorb CO_2 .

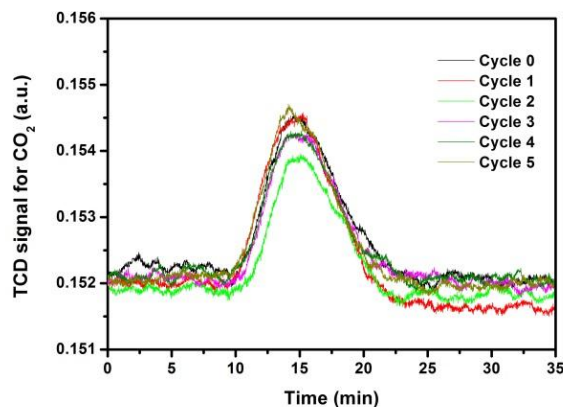


Figure 3. Five-cycle TPD profiles of CO_2 on $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{CB}[7]$ (from 50 to 150°C with a rate of $5^\circ\text{C}/\text{min}$, then kept at 150°C for 15 min).

IV. CONCLUSIONS

In summary, traditional amine absorbents for CO_2 are oftentimes corrosive to equipment and degrade through oxidation, thus severely restricting the wide application in CO_2 capture. Herein, a supramolecular approach to CO_2 capture catalyzed by CB[7] was developed. $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{CB}[7]$ complex can convert CO_2 to bicarbonate product. Advantageously, the CB[7] complex can be reused to absorb CO_2 over 5 times in solid state, thereby provides a green absorbent to CO_2 , regarding high stability, non-corrosiveness and convenient transportation.

ACKNOWLEDGMENT

This project was supported by the Fundamental Research Funds for the Central Universities, the National Natural Science Foundation of China (No. 21003123), and a grant from Advanced Programs for the Returned Overseas Chinese Scholars, Ministry of Human Resources and Social Security.

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