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Fast and Exothermic Reaction of CO_2 and Li_3N into C−N-Containing Solid Materials

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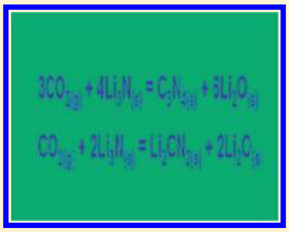
Supporting Information

ABSTRACT: The conversion of CO_2 to valuable compounds, which is considered as an effective approach to solve the global warming, represents a great challenge due to the high stability and low reactivity of CO_2. Herein, thermodynamic calculations predicted the feasibility of exothermic reactions between CO_2 and Li_3N into two important solid materials—carbon nitride and lithium cyanamide. Furthermore, the feasibility was confirmed by experiments, namely, the fast reaction between CO_2 and Li_3N produced crystal lithium cyanamide and amorphous carbon nitrides. This provides a novel process to control CO_2 emissions.



1. INTRODUCTION

The increase of atmospheric CO_2 has been identified as the primary cause for the observed warming over the past century.[1,2] There are several technological options for sequestration of atmospheric CO_2 into one of the other global pools,[3] including oceanic injection, geological injection, and scrubbing and mineral carbonation.[4,5] However, the cost and leakage as well as effects on sea biota are principal issues of the geological and oceanic sequestration. The utilization of CO_2 is being considered as a more attractive solution to solve CO_2 issues. In recent years, carbon dioxide has found growing application as a fluid in various industrial processes.[6−8] However, in those processes, CO_2 is recovered as such at the end of the application. The ideal solution should be the conversion of CO_2 into useful materials. However, this is very difficult because CO_2 has a high stability with a low reactivity. Current research attempts to activate CO_2 are being focused on carboxylation and carbonation of organic substrates,[9−11] synthesis of energy-rich C1 compounds,[12,13] photochemical conversion,[14,15] and electrochemical reduction.[16,17] However, those processes, which are endothermic, require energy input.

So far, five types of carbon nitrides have been predicted, i.e., a two-dimensional g-C_3N_4 and four three-dimensional C_3N_4 (α-C_3N_4, β-C_3N_4, cubic C_3N_4, and pseudocubic C_3N_4).[18,19] Furthermore, the three-dimensional C_3N_4 was predicted as superhard materials with structures and properties similar to those of diamond and β-Si_3N_4.[18,19] This theoretic prediction prompted worldwide interest to synthesize those attractive materials.[20−24] In most of those cases, thin films or amorphous particles with much lower nitrogen content than C_3N_4 composition were obtained.[25−28] Nowadays, the "carbon nitride" term is widely used to describe a diverse class of C−N-containing solids with nitrogen contents from a few to over 60 mol %.[25−29] Those amorphous carbon nitrides have found important uses as metal-free organocatalysts and as components of fuel cell electrodes.[30−33] Chemical synthesis of carbon nitride materials has attracted much attention. The synthetic approaches often utilized reactive precursors containing prebonded C−N core structures, such as triazine rings (C_3N_3) and related heterocyclic arenes.[34−38] On the other hand, as a fundamental class of compounds being of special importance for synthetic solid-state chemistry, cyanamides have gained increasing attention within the past decades.[39−41] Their representative is lithium cyanamide (Li_2CN_2), which is an important organic reagent[42] and a unique precursor of fertilizers.[43,44] In 1978, Pulham et al. successfully synthesized lithium cyanamide via a typical solid-state reaction of Li_2C_2 with Li_3N at 530 °C for 150 h.[45,46]

However, to our best knowledge, so far, there is not any research attempt to explore the possibility of synthesizing carbon nitrides and lithium cyanamide from greenhouse gas—CO_2. Herein, we report the fast and exothermic reaction of CO_2 and Li_3N into lithium cyanamide and carbon nitrides. This would constitute a novel approach to control of CO_2 emissions and to synthesize important N−C-containing solid materials.

2. THERMODYNAMIC ANALYSIS

First, we performed the following thermodynamic analysis (see the Supporting Information). To synthesize carbon nitrides from CO_2, CO_2 must react with an N-containing compound. The simplest N-containing compound is N_2. The reaction between CO_2 and N_2 to stoichiometric carbon nitride (C_3N_4) can be expressed as

$$3CO_{2(g)} + 2N_{2(g)} = C_3N_{4(s)} + 3O_{2(g)} \quad (1)$$

Thermodynamic calculations showed that this reaction has very positive values of enthalpy change ($\Delta H° = 1931−2075$ kJ/mol) and Gibbs free energy change ($\Delta G° = 1957−2101$ kJ/mol). Therefore, this reaction is not thermodynamically favorable. Another simple and useful N-containing compound is ammonia (NH_3). If C_3N_4 can

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be generated from CO_2 and NH_3, the following reaction should take place:

$$3CO_{2(g)} + 4NH_{3(g)} = C_3N_{4(s)} + 6H_2O_{(g)} \tag{2}$$

However, this reaction also has a very positive enthalpy change ($\Delta H° = 664-808$ kJ/mol) and Gibbs free energy change ($\Delta G° = 651-795$ kJ/mol). This means that NH_3 cannot be used for the production of carbon nitride from CO_2. Finally, lithium nitride (Li_3N) should attract our attention, because it is often used as a reactive N-source for material synthesis. If we employ Li_3N as N-source for C_3N_4 formation from CO_2, the reaction can be expressed as

$$3CO_{2(g)} + 4Li_3N_{(s)} = C_3N_{4(s)} + 6Li_2O_{(s)} \tag{3}$$

The very negative changes of its enthalpy (-853 to -997 kJ/mol) and Gibbs free energy (-752 to -896 kJ/mol) demonstrate its exothermic feature and thermodynamic feasibility, respectively. Furthermore, the reaction between CO_2 and Li_3N can also be expected to produce Li_2CN_2 as follows:

$$CO_{2(g)} + 2Li_3N_{(s)} = Li_2CN_{2(s)} + 2Li_2O_{(s)} \tag{4}$$

This reaction has a favorable thermodynamics, associated with negative values of enthalpy change (-795.9 kJ/mol) and Gibbs free energy change (-737.2 kJ/mol). Therefore, the above thermodynamic analysis predicts that the reaction between CO_2 and Li_3N would constitute a novel approach to convert CO_2 into valuable solid materials.

3. EXPERIMENTAL SECTION

Li_3N powder (purity >99.9%) was purchased from Aldrich and used as received for the experiments. A 0.3 g amount of Li_3N was loaded into a 75 cm stainless steel tube reactor (inner diameter, 5.33 mm) and then vacuumed for 3 h at room temperature. Quartz wool was used to hold Li_3N powder in the reactor. The reactor was then heated by an electrical furnace to a selected reaction temperature (250, 330, or 400 °C). Finally, at the selected reactor temperature, carbon dioxide gas (77 mL at 140 psi) was injected into the closed reactor system and the reaction between CO_2 and Li_3N started immediately. The change of CO_2 pressure was monitored with a digital pressure gauge. After the reaction of 1 h, the solid products, including crystal and amorphous materials, were obtained. Furthermore, to remove crystal solids (Li_2O, Li_2CO_3, and Li_2CN_2) from the products, the product solids were treated by 36.5 wt % hydrochloric acid (HCl), followed by washing with pure water. The remaining solid was separated from water by centrifuge. The obtained solid was then dried overnight at about 80 °C. The dried solid material is amorphous (confirmed by X-ray diffraction (XRD)).

All solid products were subjected to XRD measurements, which were carried out at 1 atm and room temperature by using a Scintag XDS2000 powder diffractometer at 45 kV and 35 mA for Cu Kα ($\lambda = 1.5406$ Å) radiation, with a scan speed of 1 deg/min and a step size of 0.03° in 2θ. The amorphous component of the solid products was further subjected to C and N elemental analysis using the CHN elemental analyzer via the combustion approach. Furthermore, the image of the amorphous component was obtained with transmission electron microscopy (TEM, JEM-4000 FX).

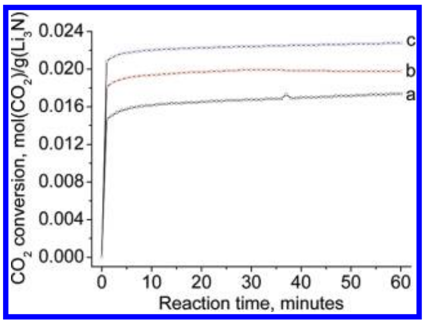

Figure 1. Conversion of CO_2 in its reaction with Li_3N at various reactor temperatures: (a) 250, (b) 330, and (c) 400 °C.

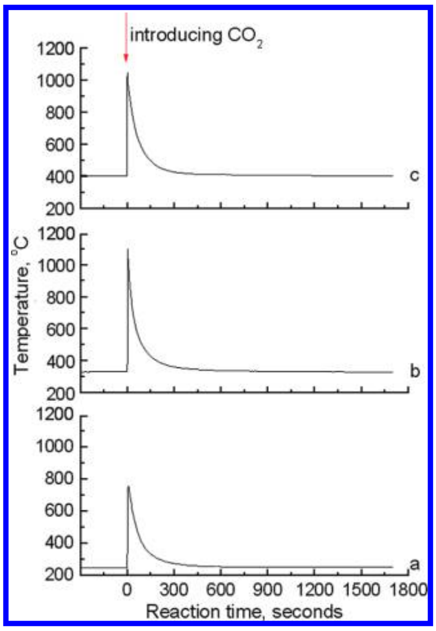

Figure 2. Temperature of Li_3N bed during reaction between CO_2 and Li_3N at various reactor temperatures: (a) 250, (b) 330, and (c) 400 °C.

4. RESULTS AND DISCUSSION

To examine the above thermodynamic prediction for synthesis of carbon nitride and lithium cyanamide from CO_2 and Li_3N, the reaction between CO_2 gas and solid Li_3N was carried out in a closed reaction system. As shown in Figure 1, one can see that the reaction is very fast. The consumed CO_2 amount increased with increasing reactor temperature. A thermocouple, which was located inside the Li_3N bed, was used to monitor the temperature change of the Li_3N bed during reaction (Figure 2). When CO_2 was introduced into the reactor at 250 °C, the bed temperature immediately jumped to 750 °C. Furthermore, when the temperature of the reactor is higher than 250 °C, the increased temperature of the material bed can reach as high as 1000 °C. The increased temperature decreased back to the initial reactor temperature in 5 min. This temperature profile indicates that the reaction, which is strongly exothermic, can be immediately ignited by CO_2 at 250 °C or higher. After the reaction (1 h), the light-yellow solid product was obtained, and then subjected to XRD measurements. The XRD measurements showed that, after the reaction, all peaks of Li_3N disappeared, whereas many new peaks occurred (Figure 3). This indicates that all of Li_3N was converted

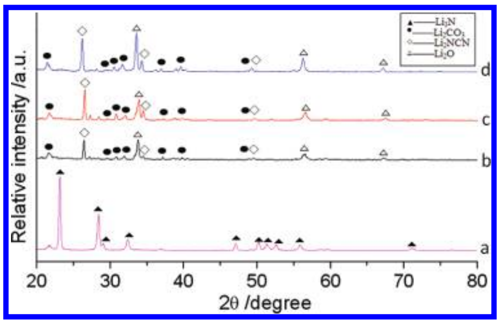

Figure 3. X-ray diffraction pattern of reactant (a, Li_3N) and solid products from reaction between CO_2 and Li_3N for 1 h at various reactor temperatures: (b) 250, (c) 330, and (d) 400 °C.

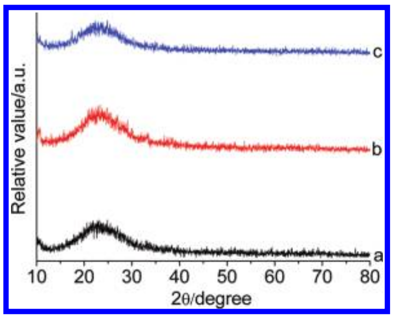

Figure 4. X-ray diffraction pattern of HCl acid-treated products from reaction between CO_2 and Li_3N for 1 h at various reactor temperatures: (a) 250, (b) 330, and (c) 400 °C.

Table 1. Content of Amorphous Product

T [a] (°C)	content[b]	N/C [c]	C_xN_y
250	7.69	1:0.80	$C_3N_{3.7}$
330	7.04	1:0.96	$C_3N_{3.1}$
400	6.12	1:1.60	$C_3N_{1.9}$

[a] Reactor temperature. [b] Amorphous content (wt %) in solid products from the element analysis.. [c] Molar ratio.

to other compounds by CO_2. Furthermore, the product obtained from the reaction has a large peak at 26.1°. Usually, this peak is used as the character of crystal g-C_3N_4 (graphite-like carbon nitride). However, after a careful analysis of the XRD patterns with the JCPDS database, we found that the large peak at 26.1° belongs to lithium cyanamide instead of g-C_3N_4. The lithium cyanamide (Li_2CN_2) with tetragonal structure has the strongest diffraction peak at 26.2° and another four strong diffraction peaks at 34.4, 40.3, 49.4, and 56.8°, respectively.[45,46] All five peaks can be found in the XRD pattern, and their relative intensities can perfectly match those of lithium cyanamide. In contrast, g-C_3N_4 should have the strongest diffraction peak at 26.5°, and other strong diffraction peaks at 46.2, 54.6, 61.2, and 87.1°.[47] Those strong diffractions cannot be found in the XRD patterns of our products. Another main component in the products is Li_2O. Furthermore, because Li_2O and CO_2 are basic and acidic, respectively, they would easily react to form Li_2CO_3 as follows:

$$Li_2O_{(s)} + CO_{2(g)} = Li_2CO_{3(s)} \tag{5}$$

This reaction can be further supported by its negative values of enthalpy change ($\Delta H° = -226$ kJ/mol) and Gibbs free energy change ($\Delta G° = -177$ kJ/mol). Indeed, the XRD patterns showed the existence of Li_2CO_3 (Figure 3). This indicates that the reaction between CO_2 and Li_3N provides a fast and energy-efficient approach for the preparation of Li_2CN_2, which proves the above thermodynamic prediction.

Although no crystal carbon nitride was observed from the XRD patterns, we can still expect amorphous carbon nitrides. To find amorphous carbon nitrides, we used an aqueous solution of HCl to dissolve all of the crystal components (Li_2CN_2, Li_2O, and Li_2CO_3) in the products at room temperature, followed by solid−liquid centrifuge separation (including pure-water wash). After the treatment, about 6−8 wt % of the solid products, which are dependent on the reactor temperature, still remained (Table 1). The remained solid material was subjected to XRD measurement. As shown in Figure 4, only one very broad peak at about 25° occurs. This is a typical characteristic of an amorphous layer structure. Furthermore, the amorphous solid was further subjected to elemental analysis, providing C/N molar ratios (Table 1). From those results, one can conclude that amorphous carbon nitride (C_xN_y) was formed. The composition of C_xN_y obtained from the reaction at the reactor temperature of 250 °C is $C_3N_{3.7}$, which is close to stoichiometric carbon nitride (C_3N_4). However, the nitrogen content of the amorphous carbon nitride decreased with increasing reactor temperature. Furthermore, the morphology of the obtained $C_3N_{3.7}$ was evaluated by TEM. As shown in Figure 5, one can see that the $C_3N_{3.7}$ possesses a curved layer structure. However, it should be noted that the amount of amorphous carbon nitrides is small in the total solid products (Table 1). This happened probably because the temperature jumped to about 1000 °C due to large amount of energy released from exothermic reactions 3, 4, and 5 (Figure 2). At such a high temperature, the produced carbon nitride could react with CO_2. Therefore, to increase the yield of carbon nitrides, the increased temperature should be reduced to inhibit the reaction between carbon nitride and CO_2.

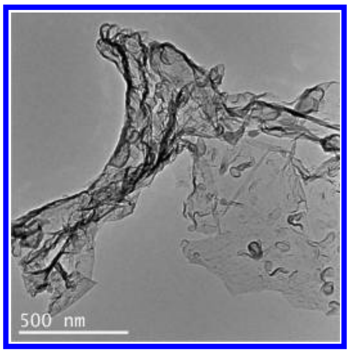

Figure 5. TEM image of carbon nitride prepared from reaction between CO_2 and Li_3N for 1 h at 250 °C.

5. CONCLUSION

In conclusion, the feasibility of exothermic reactions between CO_2 and Li_3N into carbon nitride and lithium cyanamide was predicted by thermodynamic calculations. Furthermore, the reaction experiments confirmed the prediction; namely, the fast reaction between CO_2 and Li_3N produced crystal lithium cyanamide and amorphous carbon nitrides. This provides a novel process to control CO_2 emissions.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Tables listing thermodynamic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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