Effect of Metal Ion on Ammonium Bicarbonate Solution Decomposed into Carbon Dioxide

Lu HU
School of Chemistry and Environmental Engineering, Jianghan University
Wuhan 430056, China

Hai-feng LI
School of Chemistry and Environmental Engineering, Jianghan University
Wuhan 430056, China

Mei JIN
School of Chemistry and Environmental Engineering, Jianghan University
Wuhan 430056, China

Guo-xian YU*
School of Chemistry and Environmental Engineering, Jianghan University
Wuhan 430056, China
Correspond email: guoxianyu828@yahoo.com.cn

Abstract—Ammonia-based carbon capture process is one of the promising technologies for CO2 mitigation. However, it has a problem to be solved for practical implementation due to the high volatility of ammonia, which incurs ammonia loss during regeneration. Effects of Fe3+ or Co2+ on ammonia escape and CO2 desorption in NH4HCO3 solution decomposition process were investigated. The results showed that, the addition of metal ion noticeably decreased ammonia escape and slightly increased desorption proportion due to the complexation of metal ion and free ammonia. The metal ion added also promoted desorption rate in this process. Moreover, metal ion Fe3+ is more effective than Co2+ on CO2 desorption and ammonia escape in the regeneration process.

Keywords—Fe3+; Co2+; ammonium bicarbonate; desorption; ammonia escape

I. INTRODUCTION

Carbon dioxide (CO2) is considered to be the main contributing factor to global warming and climate change. CO2 capture technologies have started getting attention[1,2]. Aqueous ammonia-based CO2 capture technology has many technical and economical advantages over amine-based capture technology, such as high CO2 absorption capacity, low regeneration energy, no sorbent degradation, cheap chemical cost, and simultaneous capture of multiple pollutants[3-10]. However, ammonia absorbent has a limitation in practical application because of its high vapor pressure, which causes high loss of ammonia in regeneration process[11]. This leads to considerable loss of ammonia and requires high cost to make up ammonia in practical implementation. Therefore, it is necessary to take appropriate measures to reduce ammonia loss and improve the economic performance.

Some measures have been reported to reduce ammonia loss, such as multistage water washing and adding organic or inorganic additives[12,13]. The former is a traditional method, and affects the water balance and consumes more energy. Metal ion additives, such as copper and zinc, have been proposed to suppress ammonia escape through their strong complexation with NH3[14,15].

In our work, the transition metals Co(II) and Fe(III) were choose to reduce ammonia loss by making use of their complexation capability with NH3. Our experimental work used ammonium bicarbonate solution to carry a regeneration and investigated the effect of metal types and metal concentration on the ammonia escape and CO2 desorption in the regeneration, and Ultraviolet absorption spectrum was used to characterize metal complexation with NH3. We hope that this study can facilitate the development of a novel method for suppressing NH3 volatilization in ammonia-based CO2 capture process.

II. EXPERIMENTAL

A. Reagent

Experimental reagent: NH4HCO3 (AR), NaOH (AR), FeCl3·6H2O (AR), CoCl2·6H2O (AR), anhydrous calcium chloride (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Concentrated sulphuric acid (AR) was purchased from Xinyang Chemical Reagent Co., Ltd. N2 (99.9%v) was purchased from Wuhan Huauerwen Industrial Co., Ltd.

B. Experimental System

Self-assembled desorption experimental system was used in the experiment, which is shown in Fig. 1. 250ml three necks flask was used as the desorption reactor, and it was fixed in a magnetic and thermostatic water bath (DF-101S, Henan Yuhua Instrument Co., Ltd., China). 100ml of NH4HCO3 with a concentration of 1.0mol/L was the reactant of this decomposition process. The decomposed gas was diluted and carried out by a stable N2. N2 flowrate was 0.8L/min, and which was controlled by a mass flowmeter(MT50-3J, Beijing HORIBA METRON Instruments Co., Ltd., China). The condenser pipe was used to cool the gas out of the solution, and thus made sure water vapor would not be taken out. Then escaped NH3 gas was...
absorbed by 50ml of 1mol/L dilute sulphuric acid when the gas mixture went through the acid pickling bottle. CO2 concentration of the gas was measured by a GC analyzer (SP-6890, Shandong Lunan Rainbow Chemical Instrument Co., Ltd., China) after which was dried by the CaCl2 drying bottle. NH3 concentration of the gas was represented by the concentration of acid from the acid pickling bottle, the concentration of acid was measured by acid-base titration method. Detail conditions of experiments was shown in Table 1.

<table>
<thead>
<tr>
<th>TABLE 1 EXPERIMENTAL CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Items</strong></td>
</tr>
<tr>
<td>Concentration of NH4HCO3 solution</td>
</tr>
<tr>
<td>Volume of NH4HCO3 solution</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>N2 flowrate</td>
</tr>
<tr>
<td>Magnetic stirring speed</td>
</tr>
<tr>
<td>Metal concentration</td>
</tr>
</tbody>
</table>

Fig. 1 Experimental system of Ammonium bicarbonate decomposition

III. RESULTS AND DISCUSSION

A. Effect of Metal Type on CO2 Flow and Desorption Proportion in the Regeneration

Effect of metal type on CO2 flow was shown in Fig. 2a. There are 2 kinds of solution containing the same molar concentration of metal, and the other kind does not contain any metal. 3 kinds of ammonium bicarbonate solution contain the same concentration of solute. CO2 flow was recorded during the reaction from starting up to 60 min, and it is seen that the flow of CO2 desorbed from the solution fast increased first and decreased later, reaching the maximum at about 2 min, and from 2 min to 10 min the flow fast decreased and then did very slowly until 60 min. From the height of the curve to the time axis, from starting up to 10 min, the order of the flow of CO2 desorbed is as follows: Fe3+ > Co2+ > without any metal.

Effect of metal type on CO2 desorption proportion was shown in Fig. 2b. It can be seen, CO2 desorption proportion was enhanced by the addition of metal, and the proportion with Fe3+ is higher than that with Co2+. Desorption proportion of the blank NH4HCO3 solution was found to be 7 % at 70 °C and that with Co2+ was increased by 0.16% and that with Fe was increased by 0.94%.

There is a reversible reaction between NH4HCO3 and NH3, H2O and CO2 in the ammonium bicarbonate solution, and metal ion in the solution, such as Fe3+ and Co2+, can produce stable complexes with free ammonia in the solution, which leads to the reaction moving to the right. FeCl3 and CoCl2 were used to investigate the effect of transitional metal ion on the regeneration. Chlorinespecies has little effect on CO2 desorption [16], so the effect of Cl on CO2 desorption can be neglected. According to Fig. 2a and Fig. 2b, the results showed that the transitional metal can enhance CO2 desorption rate and proportion by adding it to the solution, and the higher the valence state of the transition metal ions is, the better promoting efficiency is.

B. Effect of Metal Type on Ammonia Escape in the Regeneration

Effect of metal type on ammonia escape was shown in Fig. 3. It can be seen, in 20 minutes, ammonia escape seemed to be no different, but from 20 min to 60 min, ammonia escape was decreased by the additive of metal obviously. And ammonia escape with Fe3+ is lower than that with Co2+. Compared with no additive, ammonia escape was decreased by 4.90% with Co2+ and that with Fe3+ was decreased by 5.94%.

Metal ion added can complex with free ammonia to form an intermediate product [Metal(NH3)X]n+, which reduced free ammonia concentration effectively in the
solution, thus reducing ammonia escape. According to Fig. 3, transition metal ion Co^{2+} and Fe^{3+} might both have the ability to complex with free ammonia in the solution to decrease ammonia escape. And under these conditions, Fe^{3+} seems to be more effective than Co^{2+} in ammonia control.

C. Effect of Metal Concentration on CO\textsubscript{2} Flow and Desorption Proportion in the Regeneration

Effect of Fe\textsuperscript{3+} concentration on CO\textsubscript{2} flow was shown in Fig. 4a. CO\textsubscript{2} flow was recorded during the reaction from starting up to 60 min. It can be seen, CO\textsubscript{2} flow increased first and decreased later with the increasing of Fe\textsuperscript{3+} concentration from 0 to 0.03 mol/L the solution, reaching the maximum at about 2 min. Compared with no additive, Fe\textsuperscript{3+} added can accelerate the desorption rate in the beginning of reaction, and the higher Fe\textsuperscript{3+} concentration was, the greater the desorption rate was. Effect of Co\textsuperscript{2+} concentration on CO\textsubscript{2} flow was shown in Fig. 4b, and the Co\textsuperscript{2+} concentration effect is similar to Fe\textsuperscript{3+}.

Effect of metal concentration on CO\textsubscript{2} desorption proportion was shown in Fig. 5. It can be seen, CO\textsubscript{2} desorption was improved with the increasing of metal concentration, and desorption proportion with Fe\textsuperscript{3+} was higher than that with Co\textsuperscript{2+} generally. It was probably because the higher metal concentration was, the more free ammonia complexed, the greater desorption proportion was.

D. Effect of Metal Concentration on Ammonia Escape in the Regeneration

Effect of metal concentration on ammonia escape was shown in Fig. 6. It can be seen that ammonia escape increased with the increasing of time. Also, compared with no additive, metal additive significantly decreased the amount of ammonia escape. The higher concentration of metal additive was, the less ammonia escape was. According to the Fig. 6a and Fig. 6b, under the experimental condition, ammonia escape of the blank NH\textsubscript{4}HCO\textsubscript{3} solution in 60 min was found to be 41.86%, that with Fe\textsuperscript{3+} which concentration from 0.01 mol/L to 0.03 mol/L was decreased by 5.94%, 6.68%, 8.17%, and that with Co\textsuperscript{2+} was decreased by 4.93%, 5.93%, 6.89%.

E. UV-Vis Characterization

Analysis results of ammonia water, 0.01 mol/L FeCl\textsubscript{3} solution, and the mixture of both was shown in Fig. 7a, that of ammonia water, 0.01 mol/L CoCl\textsubscript{2} solution, and the mixture of both was shown in Fig. 7b. Compared with pure ammonia solution, the solution mixing with FeCl\textsubscript{3} and CoCl\textsubscript{2} had a significant increase in UV absorption intensity, indicating that its chromophore differs from the ammonia solution. The reasons are that Fe\textsuperscript{3+} and Co\textsuperscript{2+} complex with NH\textsubscript{3} to form [Fe(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{3+} and [Co(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{2+}, causing the absorption intensity increase\textsuperscript{[17]}. Therefore it can be determined that Fe\textsuperscript{3+} and Co\textsuperscript{2+} can complex with free ammonia in solution, thereby reducing ammonia volatilization.
IV. CONCLUSIONS

Effects of Fe³⁺ or Co²⁺ on ammonia escape and CO₂ desorption in NH₄HCO₃ solution decomposition process were investigated in this work. The results showed that the desorption proportion process was promoted and ammonia escape of that was inhibited by adding Fe³⁺ or Co²⁺ due to the complexation of metal and ammonia. Uv-vis spectrophotometer was used to verify ammonia escape inhibition mechanism. Meanwhile, metal additive added can accelerate the desorption rate, thus reduce desorption time and energy consumption. Two kinds of additive used in this study, Fe³⁺ is better than Co²⁺ in CO₂ desorption proportion and ammonia escape control.

ACKNOWLEDGMENT

This work was financially supported by Wuhan Planning Project of Science and Technology (No. 20150617 01011597).

REFERENCES


