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

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Abstract—Ammonia-based carbon capture process is one of the promising technologiesfor CO_2 mitigation. However, it has a problem to be solved for practical implementation due to the high volatilityof ammonia, which incurs ammonia lose during regeneration. Effects of Fe^{3+}or Co^{2+}on ammonia escape and CO_2desorption in NH_4HCO_3 solution decomposition processwere 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 Fe^{3+} is more effective than Co^{2+} on CO_2desorption and ammonia escape in the regeneration process.

Keywords-Fe^{3+}; Co^{2+}; ammonium bicarbonate; desorption; ammonia escape

I. INTRODUCTION

Carbon dioxide (CO_2) is considered to be themain contributing factor to global warming and climate change,CO_2capture technologies have started getting attention[1],2].Aqueous ammonia-based CO_2capture technology has many technical and economical advantages over amine-based capture technology, such as high CO_2absorption 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 highloss of ammonia in regeneration process[11]. This leads to considerable loss of ammonia and requires high cost to make up ammonia inpractical 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 lose, such as multistage water washing and adding organic or inorganic additives[12],13]. The former is a traditional method, and affects thewater 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 NH_3[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 NH_3. Ourexperimental work used ammonium bicarbonate solution to carry a regeneration and investigated the effect of metal types and metal concentration on the ammonia escape and CO_2 desorption in the regeneration, and Ultraviolet absorption spectrum was used to characterize metal complexation with NH_3.We hope that this study can facilitate the development of a novel method for suppressing NH_3volatilisation inammonia-based CO_2capture process.

II. EXPERIMENTAL

A. Reagent

Experimental reagent: NH_4HCO_3 (AR), NaOH (AR), $FeCl_3{\cdot}6H_2O$(AR),$CoCl_2{\cdot}6H_2O$ (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, N_2 (99.9%v) was purchased from Wuhan Huaerwen Industrial Co.,Ltd.

B. Experimental System

Self-assembled desorption experimental system was used in the experiment, which is shown inFig. 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 NH_4HCO_3 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 N_2, N_2 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 escapedNH_3 gas was

absorbed by 50ml of1mol/L dilute sulphuric acid when the gasmixture went through the acid pickling bottle.CO_2concertration of the gaswas measured by a GC analyzer (SP-6890, Shandong Lunan Rainbow Chemical Instrument Co.,Ltd.,China) after which was dried by the $CaCl_2$ drying bottle.NH_3concertration of the gaswas represented by the concertration of acid from the acid pickling bottle,the concertration of acid was measured byacid-base titration method. Detail donditions of experiments was shown inTABLE1.

TABLE1EXPERIMENTAL CONDITIONS

Items	Value
Conccentration of NH_4HCO_3 solution	1.0 mol/L
Volume of NH_4HCO_3 solution	100ml
Temperature	70℃
N_2flowrate	0.8 L/min
Magnetic stirring speed	200 r/min
Metal concentration	0-0.03 mol/L

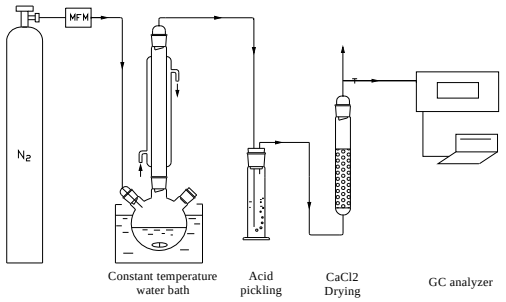
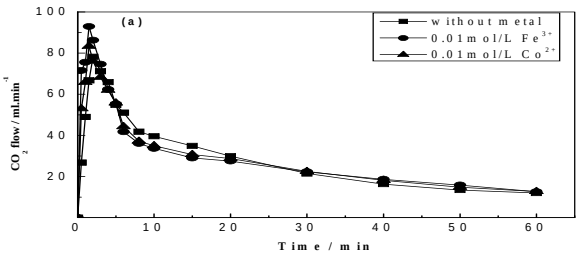


Fig. 1Experimental system of Ammonium bicarbonate decomposition

III. RESULTS AND DISCUSSION

A. Effect of Metal Type on CO_2Flow and Desorption Proportion in the Regeneration

Effect of metal type on CO_2 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. CO_2 flow was recorded during the reaction from starting up to 60 min,and it is seen that the flow of CO_2 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 CO_2 desorbed is as follows: Fe^{3+}> Co^{2+}> without any metal.



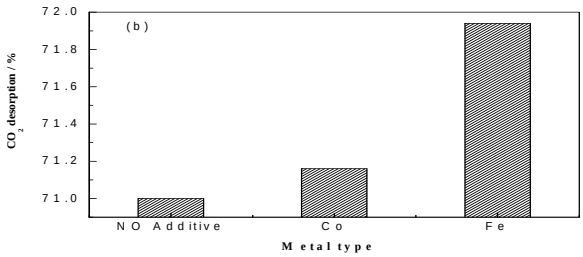


Fig. 2Effect of metal type on NH_4HCO_3 decomposition

Effect of metal type on CO_2desorption proportion was shown in Fig. 2b. It can be seen, CO_2 desorption proportion was enhanced by the addition of metal, and the proportion with Fe^{3+} is higher than that with Co^{2+}. Desorption proportion of the blank NH_4HCO_3 solution was found to be 7Fig. 21.0% at 70 ℃ and that with Co^{2+} was increased by 0.16% and that with Fe was increased by 0.94%.

There is a reversible reaction between NH_4HCO_3 and NH_3, H_2O and CO_2 in the ammonium bicarbonate solution, and metal ion in the solution, such as Fe^{3+} and Co^{2+}, can produce stable complexes with free ammonia in the solution, which leads to the reaction moving to the right. $FeCl_3$ and $CoCl_2$ were used to investigate the effect of transitional metal ion on the regeneration. Chlorinespecies has little effect on CO_2 desorption[16], so the effect of Cl^-on CO_2 desorption can be neglected. According to Fig.2a and Fig.2b, the results showed that the transitional metal can enhance CO_2 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 20min to 60min, ammonia eacape was decreased by the additive of metal obviously. And ammonia eacape with Fe^{3+} is lower than that with Co^{2+}. Compared with no additive, ammonia escape was decreased by 4.90% with Co^{2+} and that with Fe^{3+} was decreased by 5.94%.

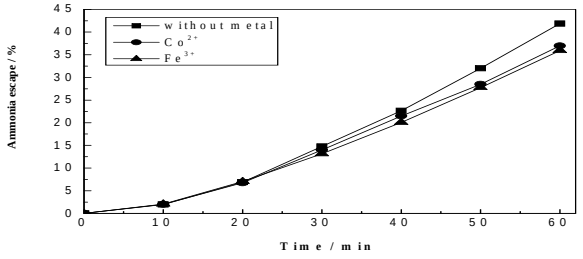


Fig. 3Effect of metal type on ammonia escape

Metal ion added can complex with free ammonia to form aintermediate product $[Metal(NH_3)x]^{n+}$, 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_2Flow and Desorption Proportion in the Regeneration

Effect of Fe^{3+} concentration on CO_2 flow was shown inFig. 4a.CO_2 flow was recorded during the reaction from starting up to 60 min. It can be seen, CO_2 flow increased first and decreased laterwith the increasing of Fe^{3+} concentration from 0 to 0.03mol/L the solution, reaching the maximum at about 2 min. Compared with no additive, Fe^{3+} added can accelerate the desorption rate in the beginning of reaction, and the higher Fe^{3+} concentration was, the greater the desorption rate was. Effect of Co^{2+} concentration on CO_2 flow was shown inFig. 4b, and the Co^{2+} concentration effect is similar to Fe^{3+}.

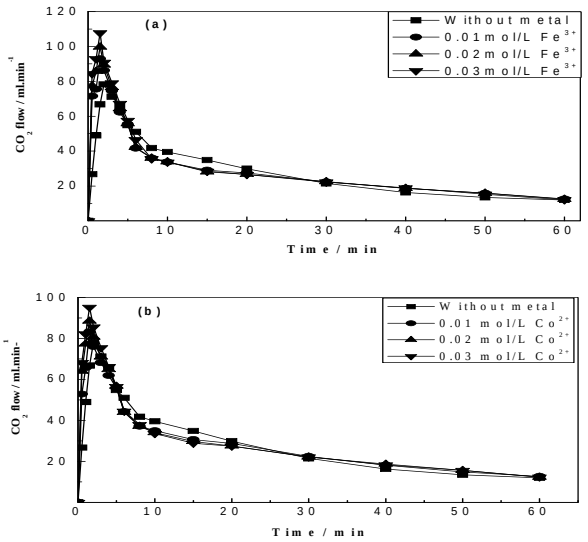


Fig. 4Effect of metal concentration on CO_2 flow

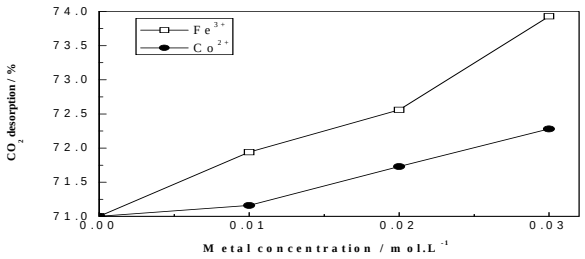


Fig. 5Effect of metal concentration on CO_2 desorption

Effect of metal concentration on CO_2 desorption proportion was shown inFig. 5. It can be seen, CO_2 desorption was improved with the increasing of metal concentration, and desorption proportion with Fe^{3+} was higher than that with Co^{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 inFig. 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. Accordding to the Fig. 6a and Fig. 6b, under the experimental condition, ammonia escape of theblank NH_4HCO_3 solution in 60 min was found to be 41.86%, that with Fe^{3+} which concentration from 0.01mol/L to 0.03mol/L was decreased by 5.94%, 6.68%, 8.17%, and that with Co^{2+} was decreased by 4.93%, 5.93%, 6.89%.

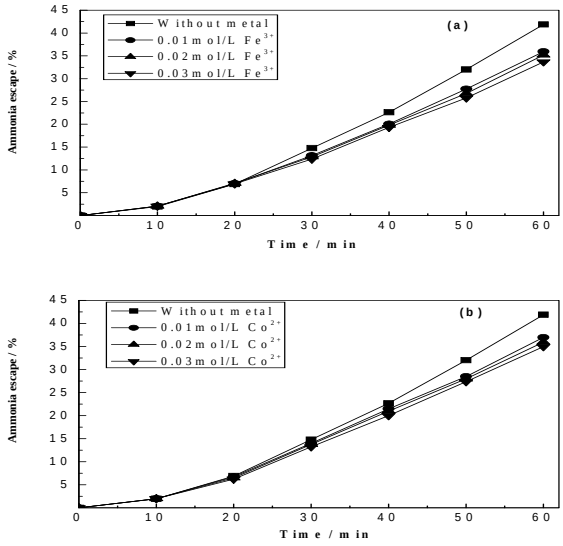


Fig. 6Effect of metal concentration on ammonia escape

E. UV-Vis Characterization

Analysis results of ammonia water, 0.01mol/L $FeCl_3$ solution, and the mixture of both was shown in Fig. 7a, that of ammonia water, 0.01mol/L $CoCl_2$ solution, and the mixture of both was shown in Fig. 7b. Compared with pure ammonia solution, the solution mixing with $FeCl_3$ and $CoCl_2$ had a significant increase in UV absorption intensity, indicating that its chromophore differs from the ammonia solution. The reasons are that Fe^{3+} and Co^{2+} complex with NH_3 to form $[Fe(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$, causing the absorption intensity increase[17]. Therefore it can be determined that Fe^{3+} and Co^{2+}can complex with free ammonia in solution, thereby reducing ammonia volatilization.

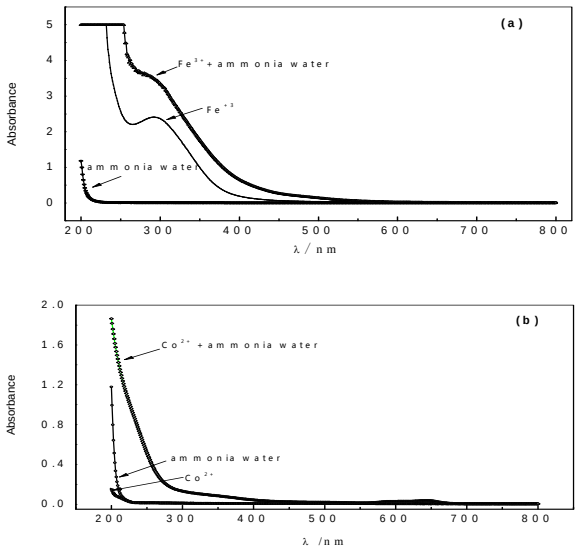


Fig. 7Ultraviolet absorption spectrum

IV. CONCLUSIONS

Effects of Fe^{3+} or Co^{2+} on ammonia escape and CO_2 desorption in NH_4HCO_3 solution decomposition process were investigated in this work. The results showed that the desorption proportionprocess was promoted and ammonia escape of that was inhibited by adding Fe^{3+} or Co^{2+} 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 comsumption. Two kinds of additive used in this study, Fe^{3+} is better than Co^{2+} in CO_2desorption proportion and ammonia escape control.

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