Ammonia Adsorption Properties of Composite Ammonia Carriers Obtained by Supporting Metal Chloride on Porous Materials

Cheng Shen, LaiHong Shen

Abstract—Ammonia is an important carrier of hydrogen energy, with the characteristics of high hydrogen content density and no carbon dioxide emission. Safe and efficient ammonia capture for ammonia synthesis from biomass is an important way to alleviate the energy crisis and solve the energy problem. Metal chloride has a chemical adsorption effect on ammonia and can be desorbed at high temperatures to obtain high-concentration ammonia after combining with ammonia, which has a good development prospect in ammonia capture and separation technology. In this paper, the ammonia adsorption properties of $CuCl_2$ were measured, and the composite adsorbents were prepared by using silicon and multi-walled carbon nanotubes, respectively to support $CuCl_2$, and the ammonia adsorption properties of the composite adsorbents were studied. The study found that the ammonia adsorption capacity of the three adsorbents decreased with the increase in temperature, so metal chlorides were more suitable for the low-temperature adsorption of ammonia. Silicon and multi-walled carbon nanotubes have an enhanced effect on the ammonia adsorption of $CuCl_2$. The reason is that the porous material itself has a physical adsorption effect on ammonia, and silicon can play the role of skeleton support in cupric chloride particles, which enhances the pore structure of the adsorbent, thereby alleviating sintering.

Keywords—Ammonia, adsorption properties, metal chloride, MWCNTs, silicon.

I. INTRODUCTION

In addition to the environmental problems caused by the emission of greenhouse gases such as CO_2, the excessive emission of ammonia (NH_3) is also one of the environmental issues that deserves to be focused on [1], [2]. NH_3 plays an important role in promoting the development of the world economy because it is used as a basic chemical in a variety of applications, including fuel cells [3], refrigeration, agriculture, energy, etc. NH_3 is an essential raw material that can be used in the manufacture of detergents, chemicals, fibers, plastics, fertilizers, and explosives. NH_3 is also an important carrier of hydrogen energy [4], with the advantage of higher hydrogen density and near-zero CO_2 emissions during hydrogen production compared to other carriers. Nitrogen fertilizer is the most produced fertilizer species in the world. Compared with other chemical fertilizer varieties, nitrogen fertilizer has greater advantages for the production of crops. NH_3 is the most important raw material for chemical nitrogen fertilizer production. The contribution rate of synthetic ammonia to food production has reached 50% [3].

According to incomplete statistics, there are 180 million tons of synthetic ammonia produced in the world every year [4]. The synthetic ammonia contributes to the production of food that feeds the 7.2 billion people on the planet. As the world's population continues to increase and the demand for synthetic ammonia expands, the production of synthetic ammonia will continue to increase to meet the needs of human survival and development. In industry, the preparation of synthetic ammonia mainly relies on the Haber method of ammonia synthesis. The main principle is to utilize the direct chemical reaction of N_2 and H_2. The working conditions are demanding, with reaction temperatures in the range of 450~550 °C and reaction pressures in the range of 200~400 atm, and iron-based catalysts need to be added for catalysis. However, due to the high temperature and high-pressure reaction environment, a large loss of energy has been caused, and a series of environmental pollution problems have also been caused. The conversion rate of synthetic ammonia is low, and the conversion rate of one reaction is only about 12%. Today, 3% of the energy consumption on earth comes from the energy loss caused by the production of synthetic ammonia in industry. In recent years, some researchers have proposed a method to synthesize ammonia from biomass, and its conversion rate is up to 56%. Therefore, the efficient separation and purification of biomass ammonia synthesis are essential [5].

There are three main technologies for the separation and purification of NH_3 [6]-[10], including cryogenic separation, membrane separation and pressure swing adsorption. The principle of cryogenic separation technology is to use the relative volatility of different gas components to compress and liquefy the mixed gas first, and then carry out rectification so that the different gas components can be separated. Membrane separation technology utilizes the difference in the permeation rate of each component in the fluid to the membrane under the driving force of concentration difference or pressure difference to realize the separation of gas components. Pressure swing adsorption separation is a key separation technology in the industry. According to the different bonding forms of the adsorption force, it can be divided into physical adsorption, chemical adsorption and selective adsorption. Among them, selective adsorption has great research and application potential due to its advantages of strong adsorption force, low energy consumption and fast regeneration of adsorbents [11].

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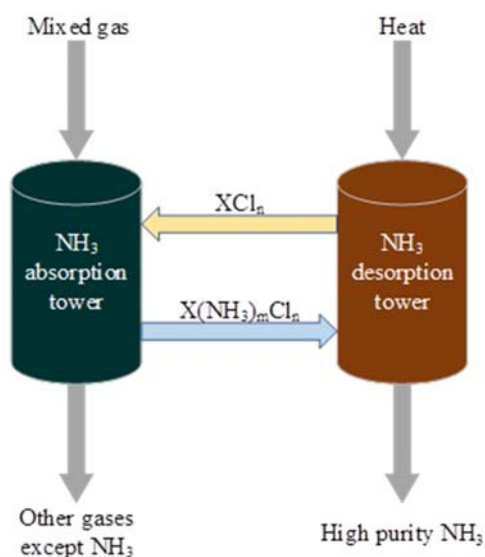Vol:17, No:11, 2023

Fig. 1 Schematic diagram of the cyclic adsorption of ammonia by metal chlorides

Metal chloride is a promising selective adsorbent, and the basic principle of its adsorption is shown in Fig. 1. Metal chlorides combine with NH_3 to form metal-ammonia complexes [12], allowing ammonia to be stored as a stable chemical species. The coordination numbers of the metal-ammonia complexes obtained by the reaction of chlorides of different metals with ammonia are different. The metal-ammine complexes are decomposed under high-temperature conditions, thereby obtaining high concentrations of ammonia and realizing the cyclic regeneration of adsorbents.

Trudel et al. [13] conducted a series of studies on the reaction between metal chlorides and ammonia and the desorption of metal-ammine complexes. It was found that the adsorption of ammonia by the adsorbent is affected by the expansion of the particle volume and changes in the atomic structure during the NH_3 adsorption reaction.

Therefore, this work proposes to prepare composite adsorbents of metal chlorides and porous materials by using silica gel and multi-walled carbon nanotubes to support $CuCl_2$, respectively. The NH_3 adsorption properties of the composite adsorbent at different temperatures and the effect of porous materials on the NH_3 adsorption capacity were studied.

II. EXPERIMENTAL SECTION

Commercial copper chloride (anhydrous, powder, purity: 99.9%) was used in the experiments. The silicon was coarse-pored spherical silicon, purchased from Nanjing Lattice Chemical Technology Co., Ltd., and its specific surface area was about 350-400 m^2/g. The multi-walled carbon nanotubes (MWCNTs) were purchased from Nanjing Wanqing Chemical Glass Instrument Co., Ltd. with a purity of more than 95% and a specific surface area of about 300-350 m^2/g.

Before preparing the composite adsorbent of silicon-supported $CuCl_2$, the silicon was heat-treated using a muffle furnace, and the silicon was pretreated at a high temperature of 300 °C for 2 h to eliminate moisture and other gas impurities contained in the silicon. After the silicon was cooled to room temperature, a certain mass of silicon was weighed and added to the salt solution of $CuCl_2$, and the mass ratio of $CuCl_2$ and silicon was 8:2. The salt solution of $CuCl_2$ was prepared using a hydrous $CuCl_2$ and deionized water. Then, the mixed solution was placed in a magnetic stirrer with a constant temperature water bath and stirred at a rate of 2000 r/min at 80 °C for a certain time. After stirring sufficiently, the mixture was put into an oven to dry for 1 d. Finally, the obtained solid was ground and suitable particles were screened out for experiments. The composite adsorbent prepared by silicon-supported $CuCl_2$ was noted as: $CuCl_2/SiO_2$.

The preparation of the MWCNT-supported $CuCl_2$ composite adsorbent was similar to the previous method for preparing the silicon-supported $CuCl_2$ adsorbent. The difference was that the pretreatment temperature of MWCNTs was different from that of silicon. The MWCNTs were heat-treated at 200 °C. The purpose was to remove impurities such as moisture in the nanotubes without destroying the structure of the nanotubes. The composite adsorbent prepared by MWCNTs-supported $CuCl_2$ was noted as: $CuCl_2/MWCNTs$.

The experimental setup of NH_3 adsorption properties of different types of composite adsorbents is shown in Fig. 2. The height of the fixed bed reactor was 600 mm and the inner diameter was 16 mm. The reactor was heated and temperature controlled by an electric furnace and a temperature controller. The reaction chamber temperature was detected by two K-type thermocouples, one placed inside the reactor and the other between the reactor and the heating device. The bottom end of the reactor was 300 mm away from the air distribution plate. Gas flow was controlled by a mass flow meter. In the process of NH_3 adsorption, 100% of high-purity NH_3 was introduced and continued for 20 min to make the adsorbent fully react with NH_3. Then switch to Ar, and set the reactor to heat up to 200 °C at a rate of 10 °C/min, and then keep the temperature constant for 20 minutes to carry out the desorption process of NH_3.

A scanning electron microscope (SEM) was used to observe the microstructure of the prepared fresh adsorbents and the adsorbents after the NH_3 adsorption reaction. The phase composition of the prepared fresh adsorbents was tested by X-ray diffractometer (XRD). The specific surface area of the fresh adsorbent was also tested, which was using a Brunauer-Emmett-Teller analyzer (BET) to analyze the effect of silicon and MWCNTs on particle structure.
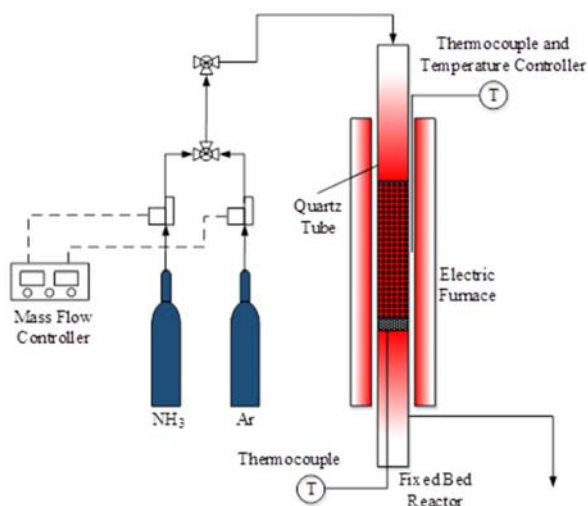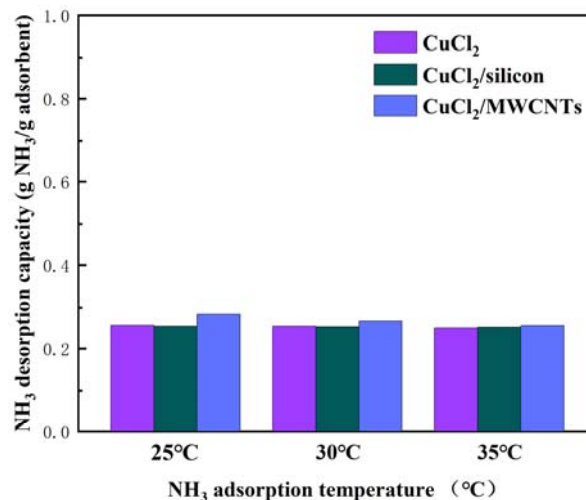
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Fig. 2 Fixed bed pedestal device diagram

III. RESULTS AND DISCUSSION

The variation of NH_3 adsorption capacity of the adsorbents with temperature is shown in Fig. 3. Within a certain temperature range, with the increase of temperature, the NH_3 adsorption capacity showed a decreasing trend. The NH_3 adsorption capacity of $CuCl_2$/MWCNTs was the highest at 25 °C, which was 0.69 g NH_3/g adsorbent, which was 4.2% higher than that of $CuCl_2$. The NH_3 adsorption capacity of $CuCl_2$/silicon was minimally affected by temperature, and the NH_3 adsorption capacity at 35 °C was only 0.0009 g NH_3/g adsorbent lower than that at 25 °C. The addition of porous materials can improve not only the NH_3 adsorption capacity of the adsorbent but also the NH_3 desorption capacity of the metal-ammine complexes, as shown in Fig. 4. Also, adsorbents with high NH_3 adsorption capacity also have high NH_3 desorption capacity.
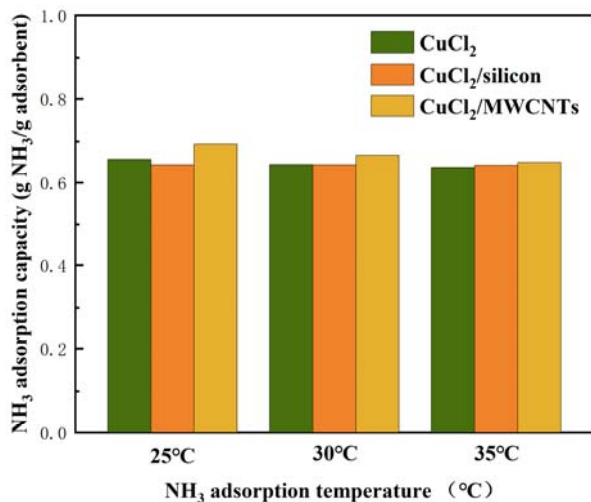

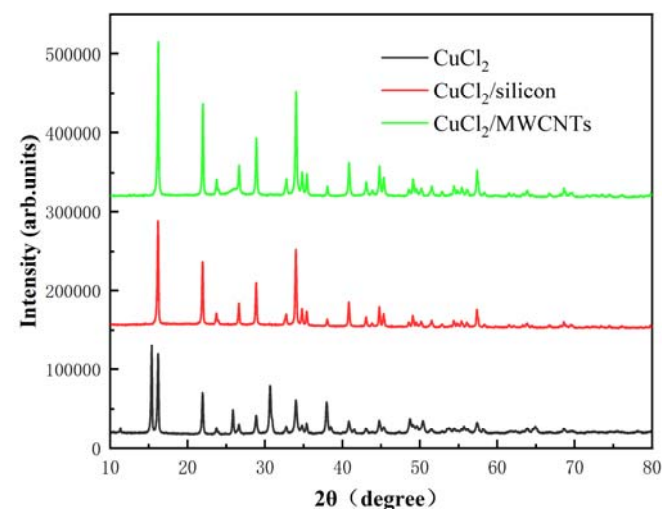Fig. 4 NH_3 desorption capacity of the adsorbents

The XRD patterns of the adsorbents are shown in Fig. 5. The addition of porous materials significantly enhanced the peak of $CuCl_2$. It could be seen from Fig. 6 that the specific surface area of $CuCl_2$/silicon had the largest specific surface area of 42.3 m^2/g, which was 2.74 times that of $CuCl_2$. The specific surface area of $CuCl_2$/MWCNTs was 168% higher than that of $CuCl_2$. The increase in specific surface area was one of the important reasons for the increase in the NH_3 adsorption capacity of the composite adsorbents.

Fig. 5 XRD patterns of the adsorbents

Fig. 3 NH_3 adsorption capacity of the adsorbents at different temperatures

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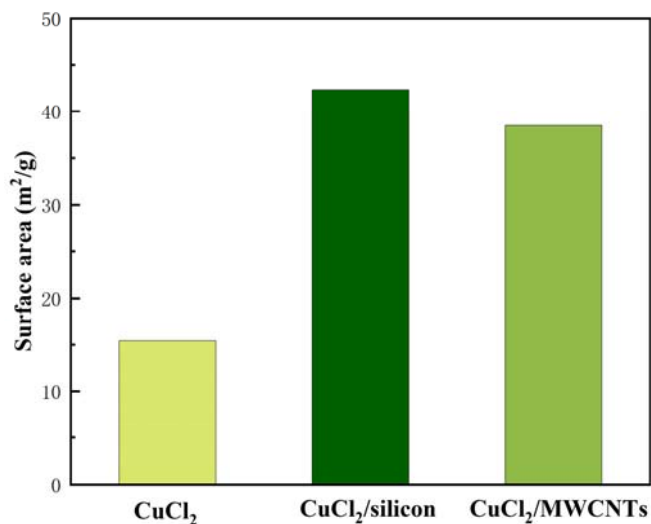International Journal of Chemical and Materials Engineering
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Fig. 6 Specific surface area diagram of the adsorbents

The apparent morphology of the adsorbents before NH_3 adsorption and after NH_3 desorption was tested, and the results are shown in Fig. 7. After the NH_3 adsorption and desorption experiments of $CuCl_2$, the particles were severely sintered, and there were almost no pores on the surface. The initial $CuCl_2$/silicon had abundant pores, and some macropores could still be seen on the surface after the NH_3 adsorption and desorption. It can be seen from Fig. 7 (e) that $CuCl_2$/MWCNTs were not uniformly dispersed in the adsorbent and were not regularly scattered in the particles. After the NH_3 adsorption and desorption process, the $CuCl_2$ particles were half wrapped around the MWCNTs and the adsorbent surface had some macropores. The structure of MWCNTs was not damaged. The increase in the number of pores also enables the composite adsorbents to have better NH_3 adsorption properties.
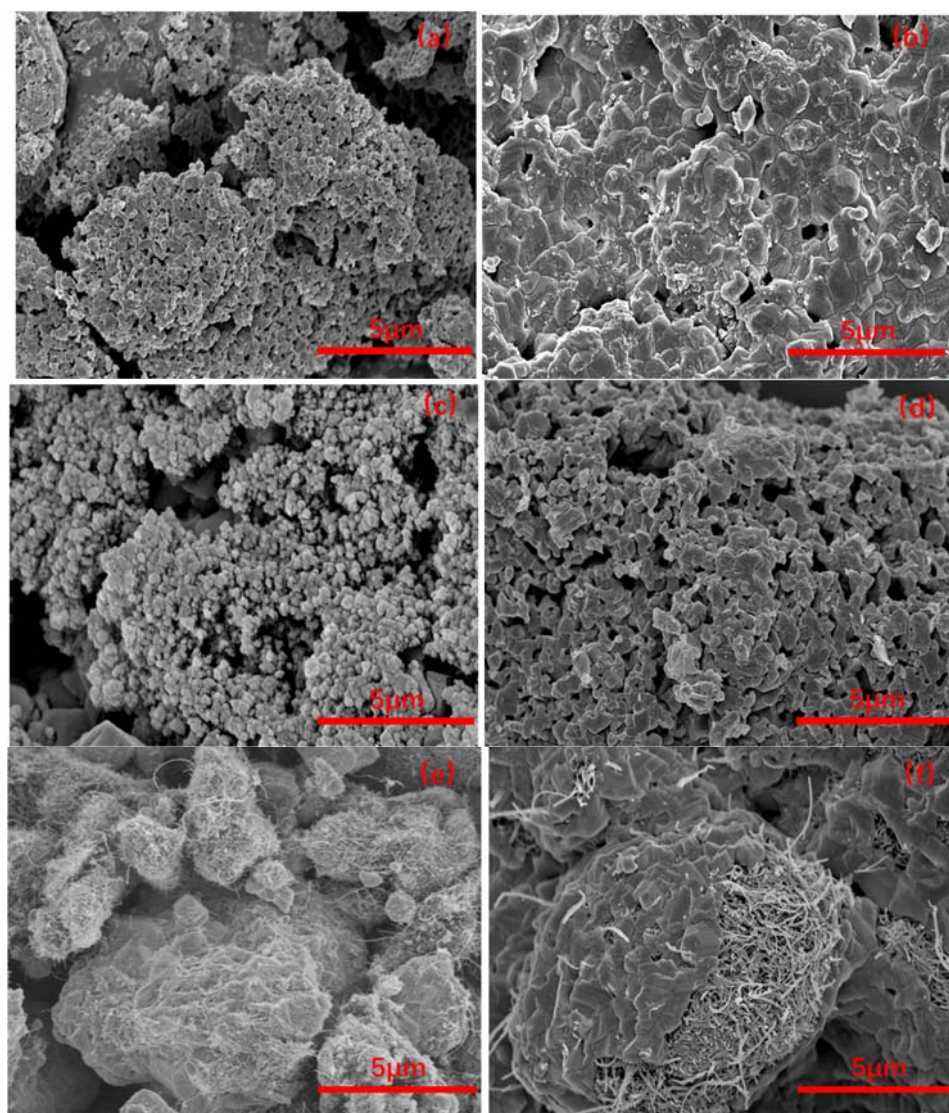

Fig. 7 SEM image of the adsorbents: (a) fresh $CuCl_2$; (b) $CuCl_2$ after NH_3 desorption; (c) fresh $CuCl_2$/silicon; (d) $CuCl_2$/silicon after NH_3 desorption; (e) $CuCl_2$/MWCNTs; (f) $CuCl_2$/MWCNTs after NH_3 desorption

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IV. CONCLUSION

In conclusion, composite adsorbents of porous material supported with metal chloride were prepared using silicon and MWCNTs, respectively. The composite adsorbents exhibited higher NH_3 adsorption capacity and more stable NH_3 adsorption properties than $CuCl_2$. The NH_3 adsorption capacity of $CuCl_2$/MWCNTs at 25 °C was as high as 0.69 g NH_3/g adsorbent, which was 4.2% higher than that of $CuCl_2$. The NH_3 adsorption capacity of $CuCl_2$/silicon at 355 cm °C was 1.008 times that of $CuCl_2$. Although the doping of silicon did not greatly improve the NH_3 adsorption capacity of $CuCl_2$, silicon played the role of skeleton support in $CuCl_2$ particles, thus alleviating the coalescence of molten salts. The supporting of porous materials increased the specific surface area of the adsorbents and enhanced the pore structure between the particles so that more NH_3 passed through the pores and contacted the surface of the adsorbent particles to achieve more NH_3 adsorption.

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