Enhanced NH₃ Adsorption Capacity of CuCl₂ by Changing the pore structure

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Abstract. Ammonia is an important carrier of hydrogen energy, with the characteristics of high hydrogen content density and no carbon dioxide emission. In recent years, many methods of ammonia synthesis using biomass have been widely studied to improve ammonia yield. Therefore, safe and efficient ammonia capture for ammonia synthesis from biomass is an important way to alleviate the energy crisis and solve the energy problem. In this paper, the NH₃ adsorption properties of CuCl₂ were measured, and the composite adsorbents were prepared by using silicon and multi-walled carbon nanotubes respectively to support CuCl₂, and the NH₃ adsorption properties of the composite adsorbents were studied. The study found that the NH₃ 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 NH₃ adsorption of CuCl₂. 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.

1 Introduction

Air pollution is one of the world's major environmental problems today, [1,2] although ammonia is also a major polluting gas. NH₃ 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. NH₃ is an essential raw material that can be used in the manufacture of detergents, chemicals, fibers, plastics, fertilizers, and explosives. NH₃ is also an important carrier of hydrogen energy, [4] with the advantage of higher hydrogen density and near-zero CO₂ emissions during hydrogen production compared to other carriers. Nitrogen fertilizer is the world's largest fertilizer production and use of fertilizer species. Compared with other chemical fertilizer varieties, nitrogen fertilizer has greater advantages for the production of crops. NH₃ is the most important raw material for chemical nitrogen fertilizer production. The contribution rate of synthetic ammonia to food production has reached 50 %.

According to incomplete statistics, there are 180 million tons of synthetic ammonia produced in the world every year. 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 N₂ and H₂. The working conditions are demanding, with reaction temperatures in the range of 450~550 ℃ 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 %. 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 NH₃, [6-10] including cryogenic separation, membrane separation and pressure swing adsorption. Cryogenic separation technology utilizes the different volatility of gases and uses compression and other techniques to separate gases with different volatility. Membrane separation technology is generally carried out at room temperature. The principle is to use the different concentration differences of the gas components. Under the driving force of this concentration difference, the gas shows different permeability to the membrane so as to realize the separation of the gas components. Pressure swing adsorption separation is a key separation technology in the industry. According to the different bonding forms of

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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]

Metal chloride is a promising selective adsorbent, and the basic principle of its adsorption is shown in Figure 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-amine 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-amine 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.
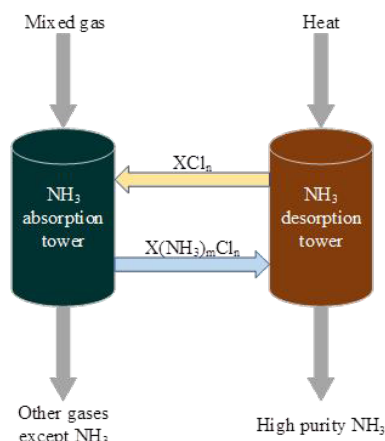

Fig.1. Schematic diagram of the cyclic NH_3 adsorption-desorption of metal chlorides.

2 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.
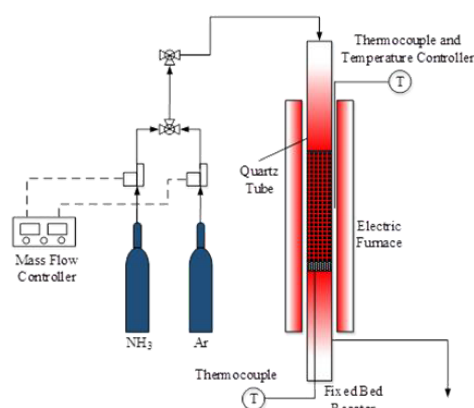

Fig. 2. Fixed bed pedestal device diagram.

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 anhydrous $CuCl_2$ 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 multi-walled carbon nanotube-supported $CuCl_2$ composite adsorbent was similar to the previous method for preparing the silicon-supported $CuCl_2$ adsorbent. The difference was that the pre-treatment temperature of multi-walled carbon nanotubes was different from that of silicon. The multi-walled carbon nanotubes 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 Figure 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 2 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 20min to make the adsorbent fully react with NH_3. Then switch to Ar, the reactor was set to heat up to 200 °C with a heating 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 multi-walled carbon nanotubes on particle structure.
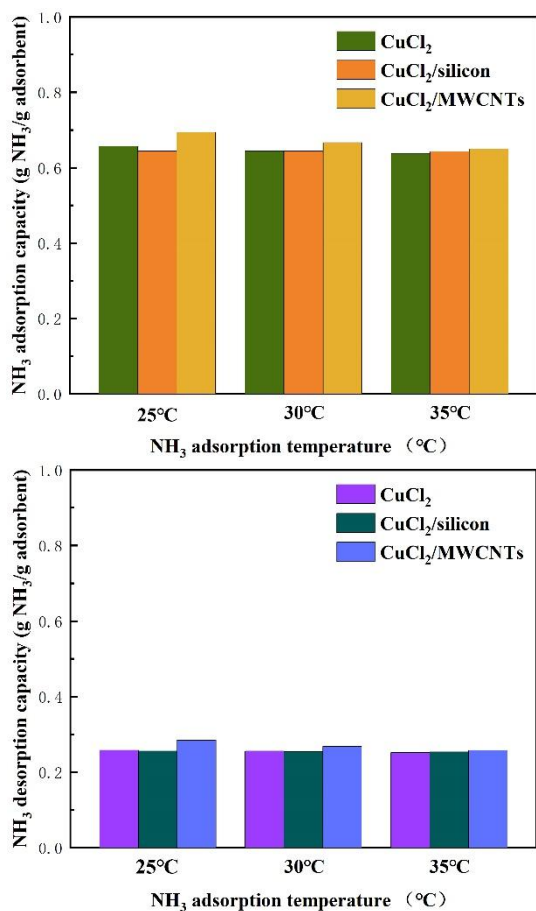
3 Results and discussion

Fig. 3. NH_3 adsorption capacity and desorption capacity of adsorbents.

The variation of NH_3 adsorption capacity of the adsorbents with temperature is shown in Figure 3. Within a certain temperature range, with the increase in 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 temperature had the least effect on the NH_3 adsorption capacity of $CuCl_2$/silicon, which was only 0.0009 g NH_3/g adsorbent lower at 35 °C than that at 25 °C.

The addition of porous materials can not only enhance the NH_3 adsorption capacity of the adsorbent but also improve the NH_3 desorption capacity of the metal-ammine complexes. Also, adsorbents with high

NH_3 adsorption capacity also have high NH_3 desorption capacity.

The change of the ammonia adsorption temperature had the greatest effect on the NH_3 desorption capacity of copper chloride modified by multi-walled carbon nanotubes, and the NH_3 desorption capacity of 25 °C was 0.2848 g NH_3/g adsorbent, which was 0.0268 g NH_3/g adsorbent higher than that of copper chloride at the same temperature and 0.029 g NH_3/g adsorbent higher than the desorption capacity of $CuCl_2$/silicon at the same temperature. The NH_3 desorption capacity of $CuCl_2$/silicon decreased by 11 % with increasing temperature.

The XRD analysis of the different adsorbents was tested, as shown in Figure 4. The addition of porous materials significantly enhanced the peak of $CuCl_2$. Among them, MWCNTs had the greatest effect on the strength of the peak of $CuCl_2$. It could be seen from Figure 5 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 $CuCl_2$. From Fig. 5, it can be inferred that the high specific surface area is one of the important reasons why the composite adsorbent modified with porous materials possesses high ammonia adsorption energy capacity.
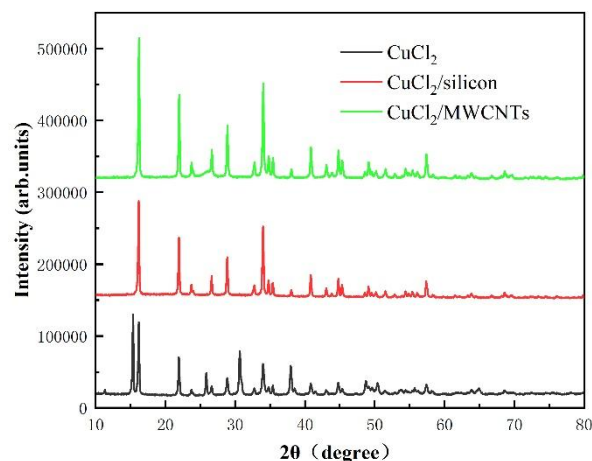

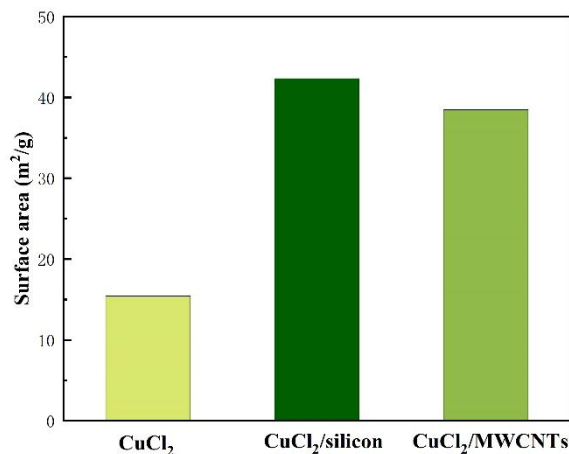**Fig. 4.** XRD patterns of the adsorbents.

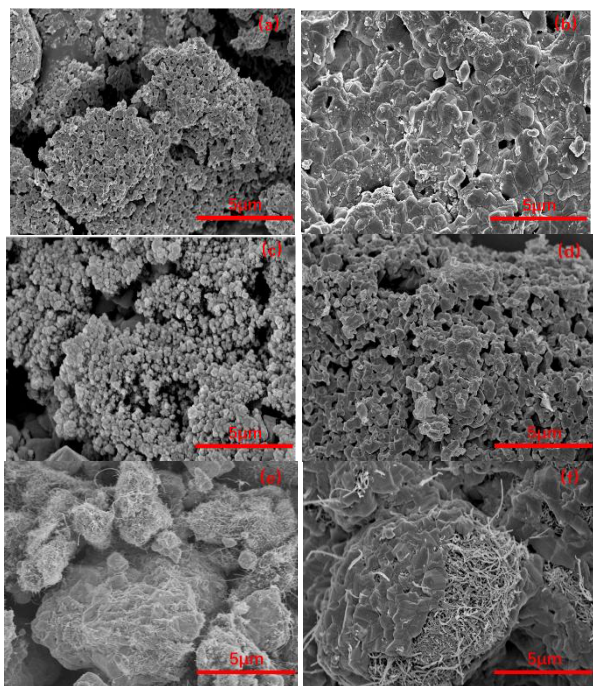**Fig. 5.** Specific surface area diagram of the adsorbents.

Fig. 6. 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).

The apparent morphology of the adsorbents before NH$_3$ adsorption and after NH$_3$ desorption was tested and the results are shown in Figure 6. 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 Figure 6 (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.

4 Conclusion

In conclusion, composite adsorbents of porous material supported with metal chloride were prepared using silicon and multi-walled carbon nanotubes, 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 35 °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.

Acknowledgments

References

1. Shen, C., Luo, C., Luo, T., Xu, J.X., Lu, B.W., Liu, S.L., Zhang, L.Q. ACS omega. 5 (29): 17908-17917 (2020)

2. Shen, C., Shen, L.H., Yan, J.C., Wang, P., Yin, X.L. Energy & Fuels. 35: 13871-13876 (2021)

3. Zamfirescu, C., Dincer, I. J. Power Sources. 185: 459-465 (2008)

4. Aoki, T., Ichikawa, T., Miyaoka, H., Kojima, Y. J. Phys. Chem. C. 118: 18412-18416 (2014)

5. Johannessen, T. US20100062296A1. (2010)

6. Mofidi, S.A.H., Udell, K.S. J. Energy Resour. Technol. 139(3): 032005 (2017)

7. Wang, Z., Yuan, X., Cong, S., Chen, A., Li, Q., Geng, F., Zhao, Z. ACS Appl. Mater. Interfaces. 10(17): 15065-15072 (2018)

8. lexander, G.B., Jan, P., Ondřej, J., Aleksandr, A.S., Lenka, Z. Procedia Engineering. 168: 231-234 (2016)

9. Qajar, A., Peer, M., Andalibi, M.R., Rajagopalan, R., Foley, H.C. Mesoporous Mater. 218: 15-23 (2015)

10. Britt, D., Tranchemontagne, D., Yaghi, O.M. Proc. Natl. Acad. Sci. U.S.A. 105: 11623-11627 (2008)

11. Shen, C., Wang, P., Shen, L.H., Yin, X.L., Miao, Z.W. Ind. Eng. Chem. Res. 61: 8616-8623 (2022)

12. Zhang, T., Miyaoka, H., Miyaoka, H., Ichikawa, T., Kojima, Y. ACS Appl. Energy Mater. 1: 232-242 (2018)

13. Trudel, J., Hosatte, S., Ternan, M. Appl. Therm. Eng. 19: 495−511 (1999)