Preparation and Characterization of a New Composite Adsorption Materials Composed of Two Activated Alumina and Microporous Molecular Sieve and Its Adsorption Property to Water

Haoyue Zhang¹,a, Yongquan Wang²,b, Zhongbin Zhang¹,* Baolian Niu¹,c

¹School of Energy and Mechanical Engineering, Nanjing Normal University, Nanjing, Jiangsu, China
²Xiamen Tobacco Industry Co., Ltd., Xiamen City, Fujian

*Corresponding author e-mail: zhangzhongbin@njnu.edu.cn, a552120533@qq.com, b27386558@qq.com, cniubaolian@njnu.edu.cn

Abstract. In order to improve the comprehensive performance of solid adsorption desiccant for compressed air adsorption dryer and reduce the loss rate of adsorption dryer, a new type of binary composite solid adsorption material suitable for compressed air drying is put forward. This material is composed of activated alumina (matrix) and 4A molecular sieve and 13X molecular sieve respectively in the proportions of 95%/5%, 90%/10% and 85%/15%. Static characteristic analysis is first made on three macro characteristic parameters, including the compressive strength, specific surface area and static water adsorption (60%RH). Thereafter, microscopic surface morphology analysis on composite material samples are employed. Comparative analysis result shows that, for compressed air drying, the activated alumina/13x molecular sieve with the proportion of 85%/15% is better than the 90%/10% activated alumina/4A molecular sieve composite solid adsorption material.

1. Introduction

Compressed air is one of the most widely used power sources in today’s society and used in many industries such as petroleum, chemical, electric power and machinery [1-2], which accounts for 10% of industrial electricity consumption in the European Union [3-5]. Adsorbent as the "heart" of adsorption dryer, its performance plays a crucial role in the overall performance of the whole system [6].

At present adsorption dryer is generally used to silica gel, activated alumina and zeolite to the compressed air containing gaseous water adsorption. Zeolite and activated alumina are two very common physical adsorbents [7]. Zeolites are porous crystalline aluminosilicates with an ordered porosity made up of micropores (<2 nm) that can accommodate a vast amount of molecules used in industry [8]. However, activated alumina has a high compressive density but it is very brittle and has a high abrasion rate. According to the research of Collier et al., silica gel, natural zeolite, synthetic zeolite and other industrial desiccant, there is still room for improvement[9].In order to prepare materials with improved and innovated properties, one of the most used methods for accomplishing
this purpose is the synergetic combination of two or more components [10]. At present, the existing composite adsorption materials mainly include diatomite-molecular sieve composite adsorption material [11], polythiophene-molecular sieve nanocomposite [12], molecular sieve-modified silica gel [13], molecular sieve-activated carbon. Activated carbon supported activated alumina composite adsorption material and composite of some molecular sieves with metal halide. By analyzing the microstructure of 4A zeolite coating, Lucio Bonaccorsi et al. found that the zeolite material had good compatibility with the oxides formed on the metal surface [14].

In order to find adsorbent with excellent comprehensive properties for compressed air drying, respectively 95%/5%, 90%/10% and 85%/15% of activated alumina/13X molecular sieve, and activated alumina/4A molecular sieve as well as the raw material of the three kinds of single the compressive strength, specific surface area and static water adsorption (60% RH) of the three kinds of static characteristic parameters were analyzed in this paper, and then using scanning electron microscope (SEM) analysis of the material microscopic surface morphology.

2. Experimental setup

2.1. Materials and synthesis method
In this paper, activated alumina, 4A molecular sieve powder and 13x molecular sieve powder are used as raw materials. Fig.1 is a solid binary composite adsorptive material ball prepared.

![Figure 1. Solid binary composite adsorption materials.](image]

2.2. Characterization of the solid binary composite adsorption materials
The compressive strength was measured by ZQJ-II intelligent particle strength tester in laboratory (As shown in Fig.2. (a)). The static water adsorption capacity was determined by the SPX-150B-II biochemical incubator and the SPX-250BF-II biochemical incubator (As shown in Fig.2. (b)). The specific surface area of the sample was characterized by the JW-BK222 specific surface area and pore diameter tester (As shown in Fig.2. (c)).

The surface, shape and size of solid binary composite adsorbents were analyzed by JSM-5610V scanning electron microscope (As shown in Fig.2. (d)). The acceleration voltage is 10kv.

![Figure 2. Instrument for analysis and testing.](image]

3. Result and discussion

3.1. Macroscopic static characteristic parameter analysis

3.1.1. Compressive strength. Fig.3 shows the compressive strength curves of 13x and 4A molecular sieves mixed with activated alumina in different proportions. The results show that the compressive
strength of single activated alumina is as high as 245.1N, while that of single 13x molecular sieve is only 94.4N. At first, the compressive strength of the composites decreased with the increase of 13x molecular sieve ratio, but it was still higher than that of single 13x molecular sieve. After 13x molecular sieve accounted for 10% of Prida, The compressive strength of the composites increased and reached the level of 203.5N when the ratio of 13x molecular sieve was 15%. The results show that when the molar ratio of molecular sieve is 10%, it reaches the maximum pressure density of 205.1N when the ratio of molecular sieve is 10%, and then decreases with the increase of the ratio of molecular sieve to molecular sieve.

3.1.2. Specific surface area. Fig.4 shows a specific surface area curve of the composite material after the 13X molecular sieve and the 4A molecular sieve are mixed with the activated alumina according to different proportions, respectively. As can be seen from the figure, the specific surface area of the single activated alumina is relatively small and is 338.344m$^2$/g, while the specific surface area of the single 13X molecular sieve is about 621.50~747.40m$^2$/g. At the beginning, with the increase of the specific surface area of the composite with the proportion of 13X molecular sieve, when the ratio of the 13X molecular sieve to the surface area reaches 5%, the maximum value of the composite material is 388.332m$^2$/g when the specific surface area of the composite material reaches the compound, and then the trend is slowly decreased. And the specific surface area of the composite material after mixing the 4A molecular sieve and the activated alumina is lower than that of the single active aluminum oxide and the single 4A molecular sieve, and the relative maximum surface area of the composite material is 281.027m$^2$/g when the molecular sieve accounts for 5 percent.
3.1.3. Static adsorbed water (60%RH). Fig. 5 shows the static adsorbed water (60%RH) curves of 13x and 4A molecular sieves mixed with activated alumina in different proportions. The results show that the static adsorbed water (60%RH) value of single activated alumina is 14.11wt%, and the static adsorbed water (60%RH) of 13x molecular sieve is 27.92wt%. When the two materials were mixed, the static water adsorption value of the composites under the same air humidity was higher than that of single activated alumina, but lower than that of single molecular sieve, and reached the maximum when 13x molecular sieve accounted for 10% of Prida. After that, the proportion of 13x molecular sieves decreased with the increase of the proportion of 13x molecular sieves.
3.2. Microscopic surface morphology analysis (SEM characterization)

For further analysis, scanning electronic microscope (SEM) pictures of composite adsorbents are taken as shown in Fig.6. The specific surface area of activated alumina is smaller, and the addition of high specific surface area porous molecular sieve opens the pore of activated alumina to a certain extent, and increases the specific surface area of activated alumina. However, according to the comparison of the three kinds of activated alumina/13x molecular sieve composites in Fig.6, it can be seen that with the increase of molecular sieve ratio, the pores of activated alumina are partially covered. As the ratio of molecular sieve to molecular sieve increases, the specific surface area of the composite decreases gradually, and the activated alumina/4A molecular sieve composite also follows the same rule.

Because the specific surface area of 13x molecular sieve is higher than 4A molecular sieve, the specific surface area of activated alumina/13x molecular sieve component composite is higher than that of activated alumina/4A molecular sieve component composite. The particle size of 4A molecular sieve in this sample is less than 13x molecular sieve. With the increase of molecular sieve ratio, the molecular sieve is finer distributed on the activated alumina matrix, which will increase the strength of the two frameworks, although the combination of the two frameworks will be enhanced, and the size of 4A molecular sieve is smaller than that of 13x molecular sieve. However, the combination of the two molecular sieves with the activated alumina matrix is not simply attached to the surface, which makes the situation more complicated and makes the change of macro strength difficult to follow the linear law. When the composition ratio of activated alumina/4A molecular sieve is up to 90% and 10%, the effect is the best and its strength reaches the maximum value of 205.1 N; The larger 13x molecular sieves are unable to enter more pores in the activated alumina matrix. It can be observed from Fig.6.(b) that the activated alumina matrix crystallizes in large area when the proportion of activated alumina/13x molecular sieve composite is 90%/10%. So that there is no better interaction between molecular sieves and activated alumina, the macroscopic strength of the zeolites reaches the lowest value of 112.1N.
4. Conclusion

The test results show that:

The comprehensive performance of solid composite adsorption material of activated alumina/4A molecular sieve with a constituent ratio of 90%/10% is more excellent than that of 85%/15% activated alumina/13X molecular sieve. This composite adsorption material makes up for the shortcomings of single activated alumina and molecular sieve, and is more suitable for compressed air drying.

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