Study on surface modification of attapulgite

XiangLi¹, RuiYang², Detang Wang¹, GanLi¹

¹ Xuzhou College of Industrial Technology, School of Chemical Engineering, Xuzhou 221140, Jiangsu, China.
² NHWA R&D Center, Xuzhou 221116, Jiangsu, China.
*Corresponding author’s e-mail: lix911@126.com

Abstract. In this study, the surface modification of attapulgite was studied. Firstly, the experiment of acid roasting was carried out. The morphology and composition of attapulgite before and after modification were systematically studied by means of SEM, TEM and FTIR. The results showed that the optimal experimental conditions for modification were hydrochloric acid acidification, the concentration was 1 M, the acidification time was 4 h, and the temperature was 75 °C. The thermal activation conditions were determined to be 420 °C roast for 2 h. Attapulgite was successfully modified, and its specific surface area ratio increased greatly, from 144.29 m²g⁻¹ to 187.87 m²g⁻¹. In this study, the attapulgite with high specific surface area prepared is of great significance for the further use of attapulgite with high added value.

1. Introduction
Attapulgite (ATP) is a kind of clay mineral with a layered chain structure, which contains water and is rich in magnesium silicate. ATP is widely used in catalysis, chemical industry, petroleum, agriculture, animal husbandry, solar energy, and silicate industry. ATP was known as the "ten thousand soil king."[1-3]

The discovery of ATP mineral has been reported all over the world, especially in the United States, China, India, Spain, and other countries with abundant resources. Especially in the United States, ATP has the highest level of production and research and development, with high technological content and added value. In recent years, there are many researches in other countries, but the discovery and development of ATP in China is relatively late, the research and high value-added utilization are not much, and the development of new products is still in the early stage [4-7].

Research on the special physicochemical properties of ATP in catalytic materials is a hot topic in the field of chemical engineering. ATP can be used as both catalyst and carrier. The modified ATP has better application performance, which can make full use of mineral soil resources, and greatly increase the added value of ATP. It is widely used in catalysts and industrial fields, creating good economic benefits.

In this paper, ATP was studied and modified as a catalyst carrier. ATP with high specific surface area was prepared by acid activating and modifying, which is of great significance for the use of ATP with high added value.

2. Experimental

2.1. Materials
Sulfuric acid, hydrochloric acid, and silver nitrate were analytical purity and purchased from Xilong Chemical Co., Ltd, Guangdong, China. Attapulgite powder were purchased from Jiangsu Huahong Mining Chem Co., Ltd., Xuyi city, Jiangsu, China, and all the chemicals were of analytical reagent grade and used as received without further purification. All the water used in the experiment was distilled water.

2.2. Instruments
As shown in table 1, the main equipment used in the experiment is listed in the table. In addition, the experiment also used four-mouth round bottom flask, beaker, measuring cylinder and other commonly used standard glass instruments.

| Name                           | Type and specification |
|--------------------------------|------------------------|
| Thermostat water bath          | GK                     |
| Vacuum drying oven             | DZF-6050               |
| Electronic scales              | JC2003                 |
| Thermal gravimetric analyzer   | TGA-7                  |
| Electric jacket                | ZNHW                   |
| Scanning electron microscope   | S-3700N                |
| Transmission electron microscope| Tecnai G2 F20          |

2.3. Experimental methods
1) Acid activation of ATP
Natural ATP contains impurities, such as carbonates and metals, which have some mineralogical limitations and weaken the physicochemical properties of minerals, so it needs to be purified. The activity of ATP with sulfuric acid and hydrochloric acid was studied.

    The method of acid activation was appropriate amount of ATP was added to the reaction three-mouth flask, and sulfuric acid or hydrochloric acid solution of a certain concentration was added according to the solid-liquid ratio of 1:20, stirred at a certain temperature for 4 hours, filtered and washed until the PH is neutral, dried, and grinded through a 100-mesh sieve.

    2) Orthogonal experimental design
There are many factors affecting the experiment of acid activating ATP, among which orthogonal experiment is designed, the main factors are acid concentration, reaction temperature, reaction time and so on. The reaction temperature and time are determined by the number of levels in the orthogonal table (as shown in table 2). The optimal conditions are determined by examining the changes in the specific surface area of ATP.

| factor | 1 | 2 | 3 |
|--------|---|---|---|
| Time /h| 4 | 25| 0.5 |
| Temperature /℃ | 85| 75| 2 |
| Concentration /mol/L | 50| 50| 1 |

3. Results and Discussion
3.1. orthogonal experimental results
Table 3 shows the BET analysis results after acid activation of ATP. The original ATP was marked as sample 0, and the changes of specific surface area, pore size and pore volume of ATP were marked as 1, 2, ..., 9.
Table 3 Test results of BET in orthogonal experiment

| Sample | $B_{\text{specific surface area}}$ (m²/g) | $V_{\text{pore volume}}$ (cm³/g) | $S_{\text{hole size}}$ (nm) |
|--------|----------------------------------------|---------------------------------|-----------------------------|
| 0      | 144.29                                 | 0.47                            | 13.32                       |
| 1      | 172.60                                 | 0.48                            | 13.56                       |
| 2      | 168.93                                 | 0.41                            | 13.20                       |
| 3      | 156.56                                 | 0.43                            | 16.36                       |
| 4      | 162.32                                 | 0.41                            | 15.09                       |
| 5      | 165.52                                 | 0.41                            | 14.32                       |
| 6      | 187.87                                 | 0.67                            | 18.16                       |
| 7      | 155.88                                 | 0.41                            | 14.13                       |
| 8      | 152.12                                 | 0.32                            | 14.11                       |
| 9      | 173.35                                 | 0.41                            | 14.12                       |

The specific surface area of 0 was 144.29 m²/g, and the specific surface area of ATP increased after acid activation, indicating that acid activation can significantly increase the specific surface area of ATP. However, the pore volumes were different, and the pore sizes were all slightly larger than the original ATP. Therefore, acid activation of ATP can increase its specific surface area, and pore volumes were different, which may be caused by the dissolution of partial cations in the ATP molecular structure by acid activation.

The optimum experimental conditions are determined by calculating the mean value and range by orthogonal test. According to the range analysis in table 4, various factors have different degrees of influence on the change of specific surface area of ATP. The main influencing factor is acid concentration, and secondary influencing factor is reaction temperature.

Table 4 The influence of factors on specific surface area of ATP

| Test          | Factors | A (Temperature) | B (Acid concentration) |
|---------------|---------|-----------------|------------------------|
| Mean value 1  |         | 113.414         | 119.964                |
| Mean value 2  |         | 112.559         | 119.154                |
| Mean value 3  |         | 122.168         | 108.923                |
| Range         |         | 9.609           | 11.041                 |

According to the above analysis results, the acid activation effect of hydrochloric acid is better than sulfuric acid. Acid concentration 1 M, reaction temperature 75 ℃, reaction time 4 h are the best acid activation conditions.

3.2. Thermal activation of ATP

After ATP was activated by acid, the thermogravimetric analysis was performed. The heating rate was 10 ℃/min, and the temperature range was 50 ℃-800 ℃.

As shown in Fig. 1, the TGA curve has a weight loss peak between 50-150 ℃, and the mass loss rate is 3.58%, which is the surface adsorbed water. At 150-210 ℃, the mass loss rate is 2.15%, which is the channel adsorbed water. The mass loss rate at 210-350 ℃ was 5.58%, which was weak coordination crystal water. The mass loss of 350-655 ℃ is 2.13%, which is strongly coordination crystallization water. Some structural water will precipitate and cause the collapse of ATP structure [8]. According to the analysis results of TGA curve, the optimal roasting temperature of ATP is 420 ℃.
3.3. SEM analysis of acid activated ATP

The morphology changes after activation of ATP acid are mainly manifested in three aspects. First, depolymerization of mineral polymers caused by removal of impurities, and decomposition of impurity cements and carbonate minerals. The second is the cation replacement, dredges the pore channel, increases the mineral specific surface area. Third, hydrogen ion substitution reaction occurs to produce more hydroxyl functional groups, which is conducive to further condensation reaction, so as to facilitate the modification of other methods.

As can be seen from Fig. 2, ATP is activated by hydrochloric acid and sulfuric acid at the same concentration, and the samples are all particular fibre structure, indicating that neither hydrochloric acid nor sulfuric acid has damaged the crystal structure of ATP. The sample than sulfuric acid activation, the hydrochloric acid activation of intergranular carbonate impurity size shrink or even disappear, rod-shaped structure more slippery, boundary clear crystal structure, crystal rods is more dispersed, the filtrate of dissolution of Fe$^{3+}$ and Fe$^{2+}$ content is higher than that of sulfuric acid activation treatment, filtrate hydrochloric acid can better to remove impurities, make its structure more clear, hydrochloric acid activation is obviously better than the performance of sulfuric acid. This is consistent with the results of the orthogonal experiment.
3.4. FIRT analysis of ATP and acid activated ATP

The water content of ATP is mainly adsorbed water and bound water, both of which have strong absorption in the infrared spectrum. Figure 3 shows the FTIR of the raw ATP, and acid activation ATP. The peak at 3615 cm\(^{-1}\) is attributed to the stretching vibration of -OH associated with Al\(^{3+}\) cations and to -OH stretching vibration of water coordinated to Mg. The peak at 3544 cm\(^{-1}\) is attributed to stretching vibrations of -OH in (Fe, Mg)-OH and (Al, Mg)-OH. The peak intensities at 3405 cm\(^{-1}\) is attributed to the absorption band of adsorbed water. The peaks at 3615 cm\(^{-1}\) and 3554 cm\(^{-1}\) exist in the raw ATP, and then are weaker until their almost disappearance for the acid activation with 3 M hydrochloric acid, the disappearance indicates the dissolution of the carbonate impurities for appropriate concentrations of acid. The peak at 1657 cm\(^{-1}\) is related to the bound water. The peak at 1195 cm\(^{-1}\), and a broad peak 996 cm\(^{-1}\) are belonged to Si-OR \(^{[9-11]}\). In summary, the FTIR analysis confirms that acid activation of the ATP with 1 M HCl.

![Figure 3 FTIR spectra of raw ATP and acid activated ATP](image)

4. Conclusions

The acid activation was put forward to surface modification of ATP to prepare catalyst support with high specific surface area. FTIR, SEM, TGA, and EDX techniques are used for studying the catalyst support, the existence of O, Mg, K, Al, Si, and Fe in the catalyst support was confirmed. The TGA analysis experiment show that the optimal roasting temperature of ATP is 420 ℃. Compared with sulfuric acid activation, hydrochloric acid has better acid activation performance. Acid concentration 1 M, reaction temperature 75 ℃, reaction time 4 h are the best acid activation conditions. The acid activated ATP has higher purity, smooth rod-like structure, more dispersed crystals, and the specific surface area increases from 144.29 m\(^2\)g\(^{-1}\) to 187.87 m\(^2\)g\(^{-1}\).

Acknowledgement

This work was subsidised by university-level industrial research and development project (KJCCYYF2019092308), university-level teaching and research project (XGY2018A002), Undergraduate innovation research project (201913107001Y).

References

[1] Qiao G, Xin-Hui L, Kui L I, et al. Research Progress in the Development of High Value-added Products of Hermetia illucens[J]. Journal of Anhui Agricultural Sciences, 2016.

[2] Yan S, Pan Y M, Wang L, et al. Effects of Calcination Temperature on the Microstructure and Adsorption Properties of Attapulgite Microspheres[J]. Materials Science Forum, 2018, 913:907-916.
[3] Kun Z, Yuan-Rui W, Ding W, et al. Review of Research Progress of Attapulgite Materials[J]. gansu metallurgy, 2019.

[4] Wang T, Chen Y, Ma J, et al. A polyethyleneimine-modified attapulgite as a novel solid support in matrix solid-phase dispersion for the extraction of cadmium traces in seafood products[J]. Talanta, 2018, 180:254-259.

[5] Mengsa C, Yihui C, Rongrong X, et al. Application of polyethyleneimine-modified attapulgite for the solid-phase extraction of chlorophenols at trace levels in environmental water samples[J]. Analytical and Bioanalytical Chemistry, 2018.

[6] Tan L, Tan X, Ren X, et al. Influence of pH, soil humic acid, ionic strength and temperature on sorption of U(VI) onto attapulgite[J]. Journal of Radioanalytical and Nuclear Chemistry, 2018.

[7] Yan S, Pan Y M, Wang L, et al. Effects of Calcination Temperature on the Microstructure and Adsorption Properties of Attapulgite Microspheres[C]// Materials Science Forum. 2018.

[8] Jia-Gui S, Lan J, Lu-Lu S, et al. Effect of High Temperature Modified Attapulgite on Migration and Transformation of Heavy Metals in Soil[J]. liaoning chemical industry, 2019.

[9] C. Blanco, F. Gonzalez, C. Pesquera, I. Benito, Differences between one aluminic palygorskite and another magnesic by infrared spectroscopy Spectrosc. Lett. 6 (1989) 659-673.

[10] M. Suarez Barrios, L.V. Flores Gonzalez, M.A. Vicente Rodriguez, J.M. Martin Pozas, Acid activation of a palygorskite with HCl: development of physico-chemical, textural and surface properties, Appl. Clay Sci. 10 (1995) 247-258.

[11] M.S. Barrios, L.V. Gonzalez, M.A. Rodriguez, J.M. Pozas, Acid activation of a palygorskite with HCl: Development of physico-chemical, textural and surface properties, Applied Clay Science Clay Miner 10 (1995) 248-257.