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The Preparation and Characterization of Natrolite Synthetized by Purified Attapulgite

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Abstract. This paper mainly researched the hydrothermal synthesis of Natrolite, using amorphous silicon source from the purified attapulgite. The effects of silicon source, silicon aluminum ratio, crystallization time and crystallization temperature on the synthesis of natrolite were investigated. The results showed that the optimal synthesis condition of natrolite was: Hydrothermal activated ATP with NaOH was silicon source, silicon aluminum ratio was 10:1, crystallization time lasted to 72h and crystallization temperature was 150℃, the template was removed by calcining 8 hours at 550℃. The structural formula of obtained natrolite is $Na_2Al_2Si_3O_{10}$•$2H_2O$.

1. Introduction

Zeolites, a family of crystalline microporous aluminosilicate materials,its micropores are defined as pores with diameters <2nm[1]. Due to its high thermal stability, hydrothermal stability and good shape-selective ability, Zeolites is widely used in adsorption, ion exchange and catalysis[2-4]. At present, there are many methods to synthetize the zeolite, such as hydrothermal synthesis, microwave synthesis, solid phase syntheses and so on. A wide variety of zeolite include MFI, Beta, MCM-41, Natrolite ,et al. The natrolite framework is composed of T_5O_{10}(T = Si, Al, Ga, Ge...) tetrahedral units, which in the case of natrolite have a SiO_4 tetrahedron as a central polyhedron and the surrounding two SiO_4 and two AlO_4 tetrahedra in alternation to satisfy the Loewenstein rule[5].

Yongjae Lee reviewed the effect of pressure on the natrolite structure[5].The synthesis of sodium natrolite is affected by various factors, such as crystallization temperature, crystallization time, the ratio of silicon to aluminum, and the kind of silicon source.Arezo Hatamifard[6] researched that the green synthesis way of a natrolite zeolite/palladium nanocomposite ,and its application as a reusable catalyst for the reduction of organic dyes in a very short time. Siavash Bahari[7] used natrolite zeolite as a natural and reusable catalyst and the results of the present work showed the desired product in excellent yield. SB Hong [8] invented a method for selectively isolating hydrogen or helium using a natrolite-based zeolite. G.A.Mamedova[9] researched the hydrothermal synthesis of natrolite-type zeolite in the natural halloysite-obsidian system.

Attapulgite, called the palygorskite or stripe stone, is a kind of layer silicate mineral materials with silicon, aluminum, magnesium, iron, et al. The typical chemical molecular formula is that

$Mg_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$[10-12]. The unique layer chain structure and high specific surface area, enable attapulgite to have size/shape selective adsorption and catalytic function, it is used in synthesis of nano-composite adsorbents and control ling the environmental pollutants at resently years[13]. The main components of purified attapulgite by chemical or physical methods are mainly silicon and oxygen, and also contain a small amount of metal ions. Molecular sieve is synthesized by purified attapulgite as silicon source, the effects of silicon source, the ratio of Si/Al under the different crystallization temperature and the synthesized time were discussed. The aim of this paper is that the preparation and characterization of natrolite synthetized by purified attapulgite.

2. Experiment and Characterization

2.1 The Instrument and Reagent

(1) Instrument: SXC-2-13 muffle furnace; DZF - 6030 vacuum drying oven;AL204 electronic balance; HJ-4a, heating magnetic stirrer. Thermal water kettle; Vacuum suction filter machine.ASAP-2020HD88 Accelerated Surface Area and Porosimetry System.
(2) Reagents:purified attapulgite,hydrochloric acid, alumina, sodium hydroxide, TEAOH (tetraethyl ammonium hydroxide) .

2.2 The acquisition of silicon source and purified attapulgite

(1)NaOH modified ATP: A certain amount of nature attapulgite and sodium hydroxide powder mixed evenly in the crucible; The sample in the crucible is calcined at 550℃ at a speed of 1℃/min for 2 hours in a muffle furnace, then grinds after cooling. The samples are mixed with NaCl 1mol/L solution, and adjusted pH to 6 with 1mol/L HCl, filtrating, drying and standbying.
(2)Acid thermal attapulgite: 2.00g of Alkali modified attapulgite was placed in 50 mL beaker, then a certain amount of 9% (wt) of hydrochloric acid was added. The mixture was stirred well with a glass rod, then the hydrothermal acidification in the reaction kettle and sealed with PTFE lining was carried out at 180 ℃ for 12 hours. The resulting material was filtered and dried at 100 ℃. The raw attapulgite contains a certain amount of silicon source and lots of metal impurity, but metal impurity was removed after purification, the mainly rest is SiO_2.

2.3 Hydrothermal synthesis of Natrolite

Weighing the quality of purified attapulgite as silicon source, the aluminum oxide, NaOH and TEAOH in a certain proportion. The above mixture placed in a beaker by use of magnetic stirring for One hour. Natrolite was synthesized by hydrothermal crystallization from the product in autoclave at 150 ℃ for 72h,followed by calcining at 550 ℃to remove the urea template.

2.4 Characterization

Rigaku D/max-Rapid Ⅱ X - ray diffraction (XRD) analysis was used to determine the crystal phase , equipped with Cu Kα source operated at 40 kV and 40 mA with a scan rate of 8°/min, a scan step of 0.02 °;the scan range of 5°~70°. Scanning electron microscopy (SEM) analysis was performed on a Quanta-450-FEG electron micro-scope, fabricated by FEI of the UK. Nitrogen adsorption-desorption isotherms were obtained on an ASAP-2020HD88 Accelerated Surface Area and Porosimetry System.

3. Results and Discussion

3.1 NaOH modified ATP

By a certain mass ratio of ATP and NaOH mixed evenly into a muffle furnace at 550 ℃, roasting by the aforementioned method, the morphology and composition analysis by SEM and EDS, the results are as following.
Figure.1 shows that Na element is found in modified product with NaOH compared without Na ion in the original attapulgite, which indicates the composition of the substance from the skeleton is changed through roasting. In the air, the metal ion content decreased under the order: Fe > K > Mg > Al>Cu, K.

K ion as active metal elements in the framework of ATP is removed by the high temperature roasting, Cu is away from the framework because of the replaced of Na.

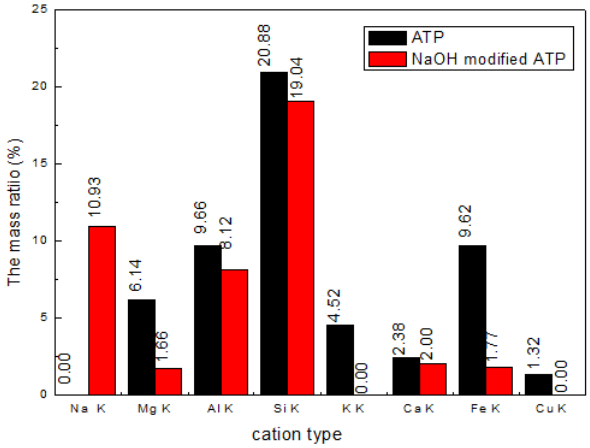

Figure.1 The composition analysis of modified product with NaOH

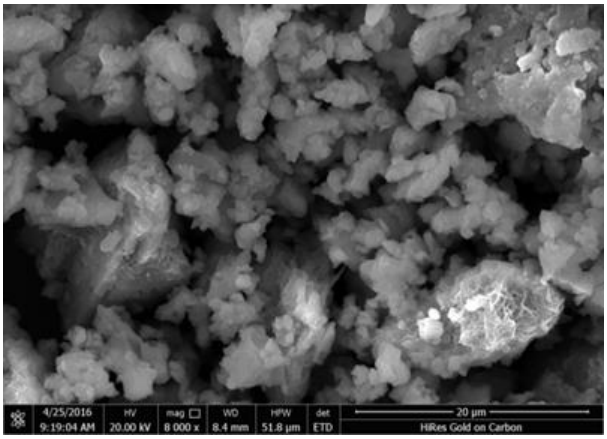

Figure. 2 SEM of modified product with NaOH in air atmosphere

From Figure.2, to observe the surface morphology of the product in 20.00kv, 4000 times, Calcined in air is granular and loosely dispersed, and the surface of a flocculent material existence.

3.2 Acid thermal the modified ATP with NaOH

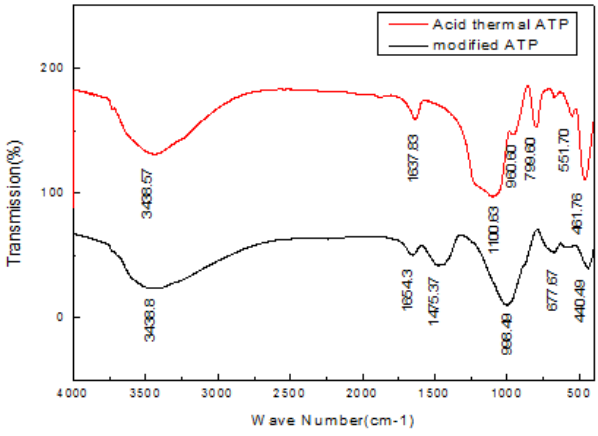

Figure.3 FT-IR analysis of activated products under hydrothermal conditions

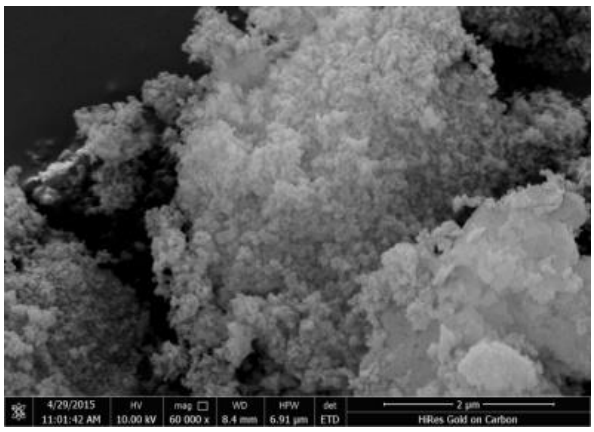

Figure.4 SEM of Acid thermal the modified ATP with NaOH

Figure.3 shows: The peak of 960.60 cm^{-1} in the graph is Si-O asymmetric stretching vibration peak, in T-O tetrahedron, reflecting the Si-O_4 stretching vibration in I direction. It proved that the basis of modified ATP with HCl and NaOH is Si and O.

From Figure.4, to observe the surface morphology of products in 10.00kv, 60000 times, the extraction of silicon source is the size of nearly spherical material, and the surface is flocculent. It shows that the existence form of silicon is amorphous state.

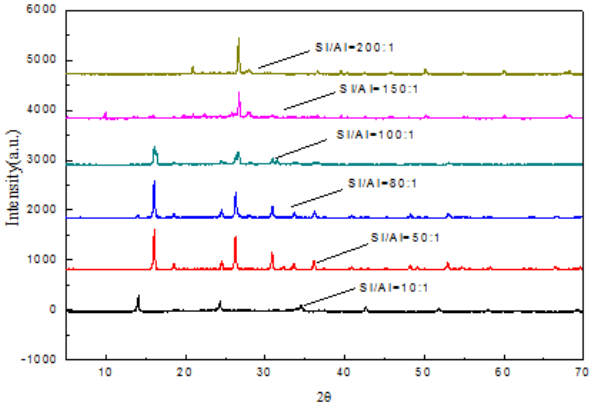

Figure.5 XRD analysis of syntheticproducts with different ratio of Si/Al

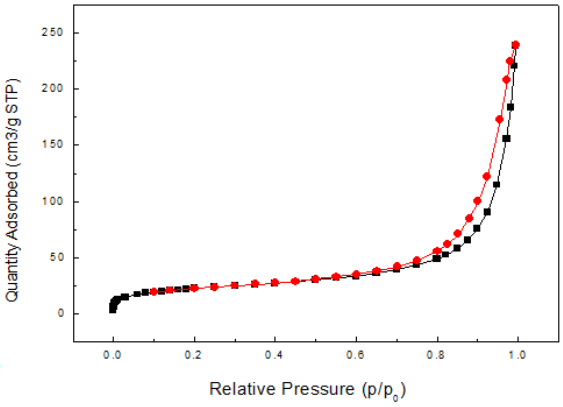

Figure.6 N_2 adsorption and desorption isotherm of Natrolite

3.3 XRD and BET analysis of Natrolite

The molecular sieve was synthesized by the above method, the structure and species were characterized by XRD as Figure.5.The XRD results: when the ratio of Si/Al is 10:1, the synthesized product is natrolite, the molecular formula is $Na_2Al_2Si_3O_{10}•2H_2O$. Strong diffraction peaks appear at 2θ=15.05, 25.72, and 43.55°, which corresponding belongs to Natrolite at (111), (440), (911), crystallographic plane.

The N_2 adsorption-desorption isotherm of Natrolite belongs to typical type-Ⅰ isotherm. Due to the strong interaction between the adsorbed material and the pore wall, the adsorption curve starts at a low relative pressure. The adsorption and desorption curves are basically the same. Single point BET specific surface area of Natrolite is 84.34 m^2/g, the average pore is 1.76nm.It belongs to microporous zeolite.

4. Conclusions

Modified ATP with NaOH in air atmosphere decrease Fe, Mg and Al while increasing the Na, K and Cu are completely removed .To purify more, the above product is hydrothermal active with HCl .The basis of Acid thermal ATP with NaOH is Si and O.XRD shows that hydrothermal activated ATP with NaOH as silicon source, Si/Al was 10:1, crystallization time was 72h and crystallization temperature was 150℃, the template was removed by calcining 8 hours at 550℃. The structural formula of obtained natrolite is $Na_2Al_2Si_3O_{10}•2H_2O$. Single point BET specific surface area of Natrolite is 84.34 m^2/g, the average pore is 2.76nm.It belongs to microporous zeolite.

5. Acknowledgements

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