

A novel double-function porous material: zeolite-activated carbon extrudates from elutrilithe

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Abstract Zeolite-activated carbon (ZEOAC) extrudates were synthesized from natural elutrilithe through a two-step process consisting of the chemical activation of elutrilithe with K_2CO_3 at 800°C followed the hydrothermal transformation in NaOH solution. During the chemical activation, carbon in elutrilithe was activated, and the kaliophilite crystalline phase with framework structure of linked (Si, Al) O_4 tetrahedra was formed simultaneously, which was then converted into zeolite A in alkaline medium. The as-synthesized samples were characterized by thermal gravimetric and differential thermal analyses (TG/DTA), N_2 adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM) and adsorptive capacities for water and hexane. The results show that this new material ZEOAC possesses the typical characteristics of zeolite and activated carbon, micro- and mesoporous structure, hydrophilic and hydrophobic properties.

Keywords Elutrilithe · Zeolite · Activated carbon · Chemical treatment · Adsorption

1 Introduction

Zeolite and activated carbon, both the most important adsorbents with a wide range of uses, have recently been increasingly used for the prevention of

environmental pollution and for meeting the constantly increasing demands for purity of natural and synthetic products. Zeolites are crystalline aluminosilicates with uniform channels/cavities and cation exchange capacity. The unique properties of zeolite, such as hydrophilic properties, high ion exchange capacity, high adsorption capacity and great selectivity, results in its many applications in the separation and purification of liquids or gases, as well as in the catalysis. Activated carbon with the large inner surface is highly porous carbon material and its amorphous skeleton consists of microcrystallites with a graphite lattice. Because of its remarkable surface properties, activated carbon can preferentially accumulate organic substances and nonpolar compounds from gaseous or liquid phase. Hence, the combination of activated carbon with zeolite is expected to enhance the property of the resulting composite for application in separation and purification technology. The composites of carbon/zeolite with corrugated structures were prepared by the in-situ crystallization of the carbonized corrugated paper and they exhibit enhanced adsorption for polar molecules because of the formation of composites of activated carbon with hydrophilic zeolites [1]. The granulated zeolite X/activated carbon composites were synthesized by carbonizing and activating and hydrothermally crystallizing the mixture of crushed rice hulls and sodium aluminate, the nitrogen adsorption and desorption isotherm of the composite showed a combined shape isotherm of types I and IV [2].

The conversion of various inorganic wastes to useful materials has been a subject of interest to many material and environmental scientists for several decades. Specifically, the hydrophobic zeolite ZSM-5 was made from the amorphous siliceous ash in low-carbon

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produced from ordinary siliceous waste materials [3, 4]. Among a variety of such wastes, increasing concern has arisen over mineral wastes because of their massive production and environmentally threatening effects. Elutrilithe, a concomitant product along with the exploitation of coal, is a typical mineral waste. Over 100 million tons of elutrilithe is produced every year in China. A great quantity of elutrilithe could cover cultivated lands and pollutes environment, so that the utilization of elutrilithe is an interesting subject. Elutrilithe contains aluminosilicate and organic carbon, and could be converted to activated carbon [5] or carbon–aluminosilicate composite adsorbent [6, 7] with adsorption properties similar to active carbon, zeolite [8], carbon–silica composite in the adsorption capacities for both water and organic compounds [9].

The aim of the present work is to attempt to convert elutrilithe into a new zeolite-activated carbon (ZEOAC) adsorbents with micro–mesoporous pore structure and double-function adsorption properties of zeolite and active carbon. The characteristics of this new material are that it is a shaped material and make full use of Si, Al and C components in raw material. Because of in a number of practical applications of the liquid and gas purification, the adsorbent must be provided in the form of granules. The self-bound (binder-free) adsorbents have several advantages in principle over those prepared conventionally from power using a binder. These shaped materials could entirely consist of active substance and thus could have a higher adsorption capacity; they may also be used directly in synthesized form without the further processing. Here, we will discuss the preparation of ZEOAC new material in a self-bound form from elutrilithe, and then characterize the samples obtained from various stages in the preparation by means of X-ray diffraction (XRD), thermal gravimetric and differential thermal analyses (TG/DTA), N_2 adsorption, scanning electron microscopy (SEM) and adsorption for water and hexane to investigate the formation process, textural structure and adsorptive properties of new material.

2 Experimental

2.1 Preparation of ZEOAC

Elutrilithe from Shanxi, China, with a chemical composition of 33.1 wt% SiO_2 , 28.8 wt% Al_2O_3 , 14.5 wt% C and 23.6 wt% other oxides (Fe_2O_3 , CaO, MgO and TiO_2 etc), water and impurity was used as raw material.

The steps involved for preparation of ZEOAC in formed shape were as follows [10]:

- (1) Chemical activation of elutrilithe: The raw material elutrilithe was crushed and sieved to a particle size smaller than 200 mesh (74 μm) and was blended with K_2CO_3 powder in the weight ratio of 1:1–2; the resulting mixtures were moistened with water and then extruded to form the cylindrical samples with size of 2×4 mm, and dried and then placed inside the center of a quartz column inside a tubular electric furnace and heated to 800°C under an inert flow of nitrogen and maintained for 3 h. The activated elutrilithe was cooled and washed with hot water.
- (2) Hydrothermal crystallization: The aluminosilicate in activated elutrilithe extrudates were converted into zeolite by hydrothermal synthesis. The activated extrudate was put into 1.5–4.0 mol/L NaOH solution in the ratio of solid/liquid (g/ml) 3–5 at 60°C for 2–6 h and then 90°C for 8–24 h under continuously stirring. The resulting products were thoroughly washed with water and dried at 120°C, zeolite 4A-activated carbon (ZEOAC-4) extrudates were obtained; zeolite 5A-activated carbon (ZEOAC-5) is prepared by ion-exchanging ZEOAC-4 in the solution of $CaCl_2$.

2.2 Characterization

X-ray diffraction (XRD) patterns of the materials synthesized in this work were recorded with a Rigaku 2500 powder diffractometer using Ni filtered CuK_{α} radiation. The morphology was studied with a JSM35C scanning electron microscopy (SEM). Thermal gravimetric and differential thermal analyses (TG/DTA) were carried out on Netzsch thermal analyzer at a heating rate of 10°C min^{-1} . Nitrogen adsorption isotherms were measured with a NOVA 1200e surface area and pore size analyzer (Quantachrome). Samples were outgassed at 300°C prior to analysis. The surface areas were calculated with the Brunauer–Emmett–Teller (BET) equation and pore size distributions were obtained using the Barret–Joyner–Halenda (BJH) method (adsorption isotherm). The volume adsorbed is corrected to standard conditions of temperature and pressure (STP).

2.3 Adsorption test

The conventional method of heating the samples at 300°C for 2 h, cooling in the desiccators and

rehydrating to the equilibrium water content was adopted for the determination of water adsorption capacity of selected samples. Nearly 1 g of the sample was accurately weighed and heated in a muffle furnace to 300°C with a holding time of 2 h. The sample was then cooled in the desiccators and weighed again. The sample was kept in a hydrator maintained at 35% relative humidity by a saturated solution of sodium chloride for 24 h and then weighed. The increase in weight due to the adsorption of water is termed as the calcined water capacity.

The benzene adsorption capacity of the sample was also measured in a flow system at 25°C under relative pressure $P/P_0 = 0.6$ (hexane vapor). Before the measurement sample was in-situ outgassed at 300°C up to 10 Pa and then cooled.

3 Results

The TG/DTA analyses of elutrilithe + K_2CO_3 (1:1) physical mixture, along with individual elutrilithe and K_2CO_3 in flowing N_2 were carried out to investigate the chemical activation process of elutrilithe. As shown in Fig. 1, the obvious differences exist between curves of the mixture and individual elutrilithe or K_2CO_3 and curves of mixture are not simple combination of the actions of elutrilithe and K_2CO_3 . In the range of temperature lower than 850°C, K_2CO_3 hydrate displays only the weight loss because of dehydration and a corresponding endothermal peak and no decomposition occurs; The raw material elutrilithe shows the loss of the weight as two effects, the first one as a weak loss between room temperature and 200°C, and the second one as a strong loss, centered at 540°C. At the same time, the DTA curves of the elutrilithe show two endothermal peaks corresponded with the two effects of weight loss. For the elutrilithe + K_2CO_3 mixture, the behavior is different. The weight loss are clearly divided into two processes, a rapid loss of weight between room temperature and 200°C, that is similar to that of K_2CO_3 , and a continuous loss of weight in the range of 200–850°C. The characteristic of DTA curve for elutrilithe + K_2CO_3 mixture is the appearance of a strong endothermal peak above 800°C.

Figure 2 shows the TG/DTA curves in air of the elutrilithe activated by K_2CO_3 (activated elutrilithe), the elutrilithe pre-dehydrated in N_2 at 800°C in the absence of K_2CO_3 and ZEOAC-4. In the DTA curves, the peaks coming of carbon burning appear at around 490°C for the activated elutrilithe and at 520°C for ZEOAC-4, whereas at 615°C for pre-dehydrated elutrilithe. The carbon content of the samples derived

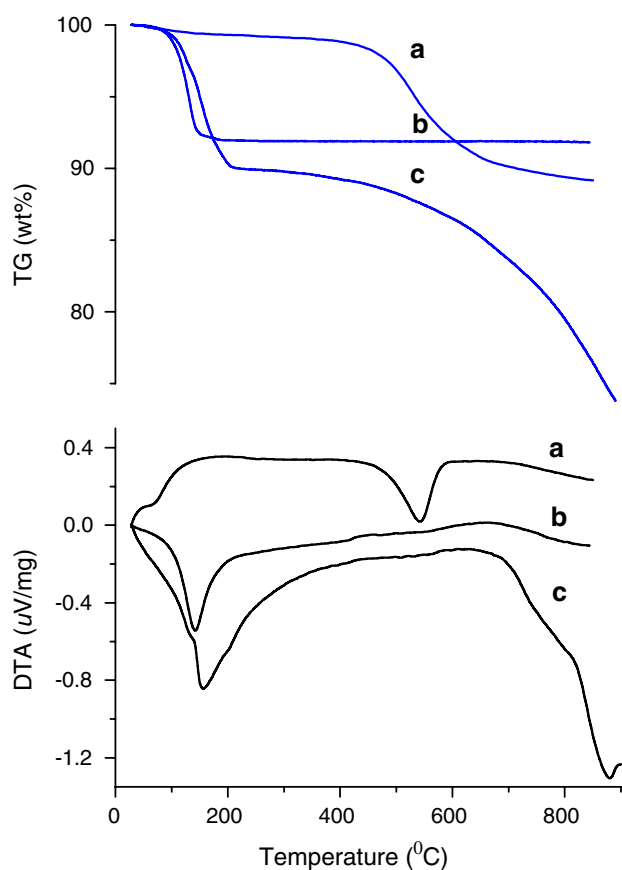


Fig. 1 TG/DTA of elutrilithe (a), K_2CO_3 (b) and elutrilithe + K_2CO_3 mixture (c) in N_2

from the weight loss in TG process reduce from 14.5% of elutrilithe to 7.5% of chemical activated elutrilithe, similar result was also found by Hu and Vansant [6, 7]. On the other hand, from their TG curves between room temperature and around 400°C, it is seen the weight loss corresponding to release of water of the samples increase from un-activated elutrilithe, activated elutrilithe to ZEOAC-4, especially for ZEOAC-4 the water content reach 14.5%.

The XRD analysis patterns of the raw material elutrilithe, activated elutrilithe and final new material product (ZEOAC-4) are illustrated in Fig. 3, and show the changes in crystalline phase during the various periods. It can be seen that the mineralogical phase of elutrilithe is composed of kaolinite as major crystalline phase along with minor quartz and smectite (Fig. 3a), which then disappear as elutrilithe is treated at high temperature in the presence of K_2CO_3 , simultaneously; crystalline kaliophilite form [11] and is observed in XRD pattern (Fig. 3b). Further, kaliophilite was hydrothermally transformed into zeolite in NaOH solution (Fig. 3c).

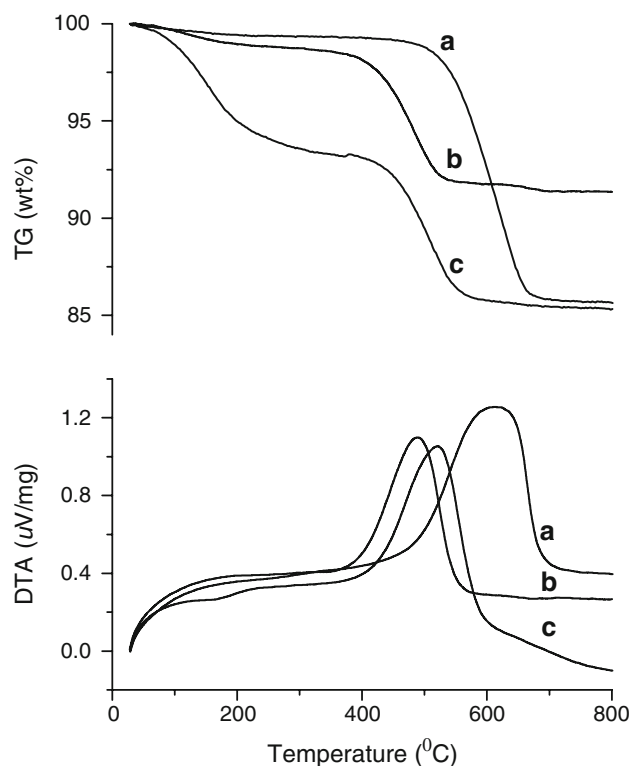


Fig. 2 TG/DTA of un-activated elutrilithe (a), activated elutrilithe (b) and zeolite 4A- activated carbon (c) in air

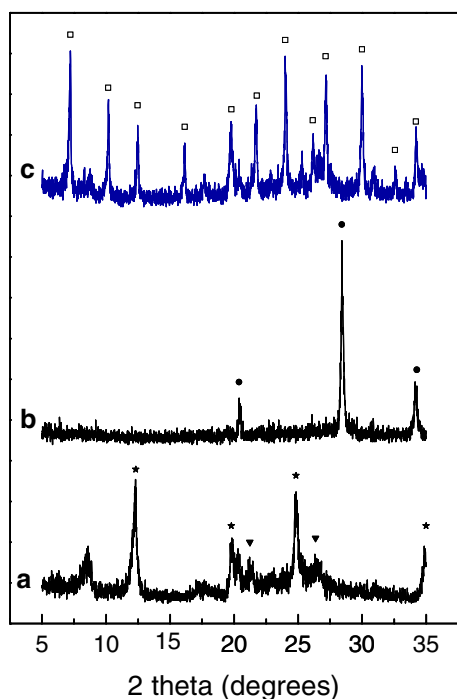


Fig. 3 XRD patterns of elutrilithe (a), activated elutrilithe (b) and zeolite 4A-activated carbon (c) ★ kaolinite, ▼ quartz, ● kaliophilite, □ zeolite A

The N_2 adsorption–desorption isotherms of the elutrilithe, activated elutrilithe and ZEOAC-5 samples, and thereby calculated BJH pore size distribution and pore structure parameters are shown in Fig. 4, 5 and Table 1, respectively. The raw material elutrilithe exhibits a type-II isotherm, a poor adsorption capacity and low surface area. The isotherm of the activated

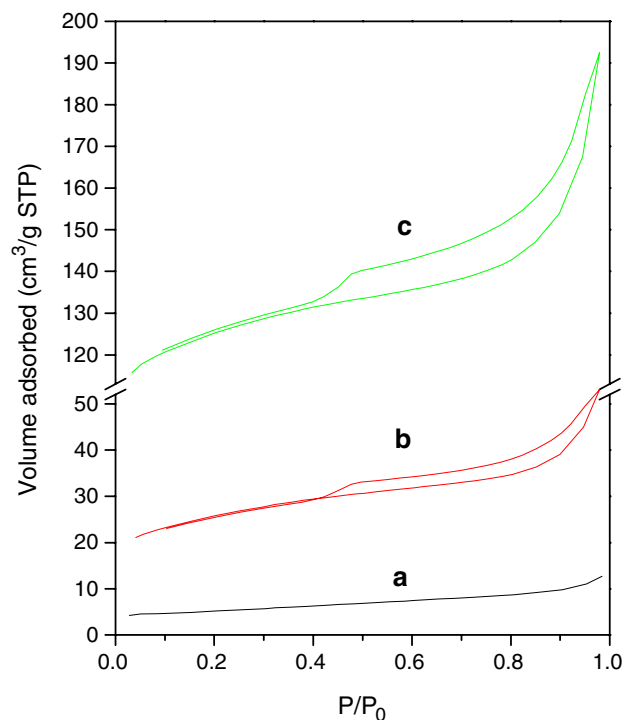


Fig. 4 Adsorption–desorption isotherms for elutrilithe (a), activated elutrilithe (b) and zeolite 5A-activated carbon (c)

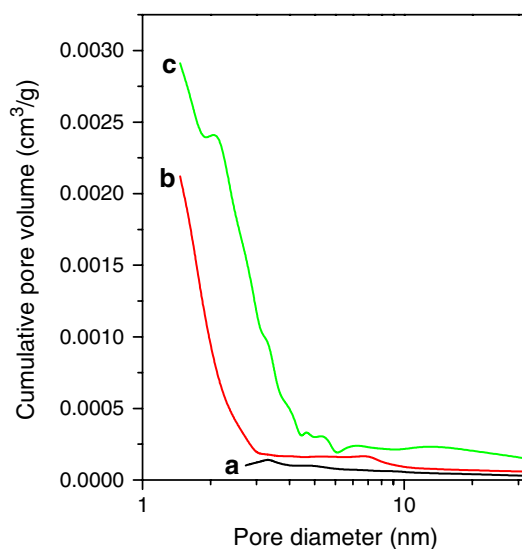


Fig. 5 BJH pore size distribution for elutrilithe (a), activated elutrilithe (b) and zeolite 5A-activated carbon (c)

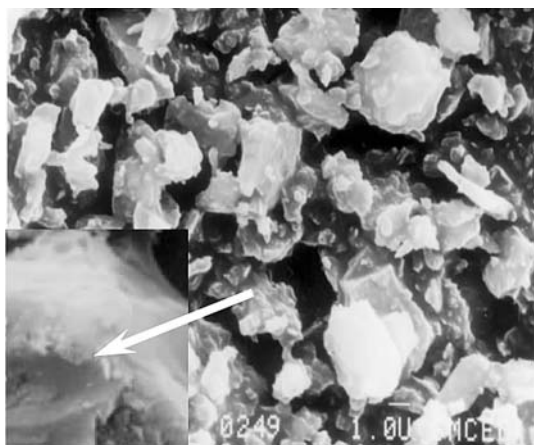
Table 1 Pore structure parameters of samples

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)		
		Total	Micropore	Mesopore
Elutrilithe	10	0.019	0.003	0.010
Activated elutrilithe	104	0.084	0.020	0.060
ZEOAC-5 ^a	386	0.298	0.159	0.140

^a zeolite 5A-activated carbon

elutrilithe appears to be a combination of the type-II isotherm and type IV isotherm. The adsorption increases rapidly at low relative pressure of <0.2, followed by a slow uptake of the adsorbent in the range of 0.2–0.4 and the steep slope at relative pressure of about 0.9; moreover, the large hysteresis loop is encountered within the relative pressure ranging from 0.45 to 1.0. This indicates the appearance of a higher percentage of mesopore and a small portion of micropore in activated elutrilithe because carbon in elutrilithe is activated, resulting in the pore volume and surface area increase obviously. The pore size distribution of activated elutrilithe is showed in Fig. 5. For new material ZEOAC-5, the shape of its adsorption isotherm is similar to that of activated elutrilithe, but the adsorption capacity increase greatly, resulting in the increase of the total surface area and pore volume; thereinto, the percentage contribution of the increase of micropore volume is higher compared to that of mesopore volume, though the absolute value of mesopore volume increases.

Figure 6 is the SEM image of a typical ZEOAC material obtained in the present investigation. The large particles represent the zeolite crystals with cubic structure and the small white patches around the zeolite crystals are the activated carbon aggregates. Multiple crystal growth is also observed in the zeolite.

**Fig. 6** SEM image of zeolite A-activated carbon**Table 2** Adsorption capacities of samples for water and hexane

Samples	Adsorption capacity (wt%)	
	H ₂ O	<i>n</i> -C ₆ H ₁₄
Elutrilithe	1.10	3.21
Activated elutrilithe	2.50	13.4
ZEOAC-4 ^a	15.6	15.3
ZEOAC-5 ^b	17.1	20.9

^a zeolite 4A-activated carbon^b zeolite 5A-activated carbon

The adsorption capacities of the raw material elutrilithe, activated elutrilithe, ZEOAC-4 and ZEOAC-5 under same condition for water and hexane, as a representative of organic nonpolar compounds, are measured and listed in Table 2. Due to its natural properties, elutrilithe presents a rather low adsorption capacity for water and organic compound. When it is treated into activated elutrilithe, its can adsorb appreciable amount of hexane. Furthermore, after the aluminosilicate in activated elutrilithe is crystallized into zeolite 4A and then converted into zeolite 5A by calcium ion-change, the adsorption capacities of new material ZEOAC-5 for water and hexane increase significantly.

4 Discussion

The chemical composition of natural elutrilithe is mainly composed of aluminosilicate and carbon. Its properties with the low surface area and poor affinity result in its low adsorption capacity while it is used as adsorbent. Chemical activation has been employed to convert elutrilithe to useful adsorbent materials. One of the methods was to modify the elutrilithe with calcium chloride or zinc chloride at high temperature to increase its surface area and corresponding adsorption capacity [7, 12]. Another method was to activate elutrilithe with potassium hydroxide to prepare the effective new material adsorbent with respect to its adsorptive capacity that is comparable with activated carbon [6]. Thereafter, because of the corrosiveness and hygroscopicity of KOH, potassium carbonate was used as to active elutrilithe, and convenient pre- and post-treatment with K₂CO₃ and acid solution, respectively were practiced to lower the ash content and to increase the surface area and porosity of activated carbon adsorbent [5]. In addition, it was found that the carbon–silica new material adsorbent with high adsorption capacities for both water and organic compounds were prepared from elutrilithe, in which the activation of carbon in elutrilithe was also carried

out with K_2CO_3 at high temperature in N_2 [9]. Hence, in the present work to prepare ZEOAC, K_2CO_3 is still used to active the carbon in elutrilithe into activated carbon. As expected, an obvious increase in the surface area, pore volume and adsorptive capacity of hexane can be observed for activated elutrilithe sample from the results displayed in Figs. 4, 5 and Tables 1, 2. Unlike the cases of elutrilithe in the absence of K_2CO_3 (Fig. 2a), the TG/DTA curves of elutrilithe with K_2CO_3 reveal the existence of interaction between carbon in elutrilithe and K_2CO_3 , so that a part of carbon of elutrilithe is consumed and corresponding pores are formed [6, 7].

Kaolinite is the major mineral component of elutrilithe, which has been showed in Fig. 3a. It is well known that the kaolinite with Si/Al ~ 1 can be conveniently used as an ideal raw material for the synthesis of low silica zeolite [13]. Usually, the synthesis of low silica zeolite from kaolinite essentially consists of two step (1) thermal preactivation of kaolinite to get a dehydroxylated X-ray amorphous product called metakaolin and (2) hydrothermal reaction of metakaolin with aqueous alkali. Because of the high passivity of kaolinite to prepare zeolite, it is necessary to obtain metakaolin by calcination of kaolinite. Kaolinite is a layer silicate composed of sheets of SiO_4 tetrahedra and AlO_6 octahedra. On heating kaolinite to metakaolin at the 750–800°C, the Al changes from 6- to 4- and 5-coordination with much higher the reactivity than AlO_6 [11], so this transformation occurs with the loss of structural water and a reorganization of structure (Fig. 1).

In the present study, when the elutrilithe is activated at 800°C by K_2CO_3 in N_2 , not only carbon in elutrilithe is activated but also kaolinite in the elutrilithe is converted into kaliophilite simultaneously. The conversion of kaolinite with K_2CO_3 is different than without K_2CO_3 , as XRD pattern shown in Fig. 3b. The crystalline kaliophilite, not amorphous metakaolin, is obtained. Like zeolite, kaliophilite has framework structure of linked (Si, Al) O_4 tetrahedra. They could be obtained by heating mixtures of kaolinite with appropriate alkali carbonate at 700°C [11] or heating zeolites of corresponding chemical composition above 950°C, and these transformation were topotactic [9]. The appearance of a strong endothermal peak above 700°C in DTA curve of elutrilithe + K_2CO_3 mixture

presented in Fig. 1 is just derived from the transformation of elutrilithe to kaliophilite. The results in present experiment show that kaliophilite crystalline, like metakaolin, can be also converted to zeolite A by the hydrothermal synthesis in alkaline medium and the activated carbon in the activated elutrilithe is preserved, consequently the ZEOAC new material is synthesized.

The characterizations of adsorption property, listed in Table 2, indicate that the new material can adsorb either water or hexane. It is noticeable that the new material has a much more adsorption capacity for hexane than zeolite 5A, reflecting the promotion effect of activated carbon on adsorption of organic compound.

In summary, the new material has the micro- and meso-porous structure and hydrophobic and hydrophilic properties because of the co-existence of activated carbon and zeolite in it. The characteristics above will be very useful for its application as adsorbent in the aspects of water treatment, separation and purification of gas or liquid. On the other hand, the synthesis of the new material provides a new reasonable route for the utilization of waste elutrilithe.

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