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# Synthesis and characterization of zeolite 4A from soft kaolin

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**ABSTRACT**

The synthesis of zeolite 4A from soft kaolin has been studied. Kaolin was converted to metakaolin by firing at 550 °C for 2 h, which was then added to NaOH solutions of appropriate concentration. The optimum molar ratios for the main constituents in the starting gel were $SiO_2/Al_2O_3$ = 1.7, $Na_2O/SiO_2$ = 2.8 and $H_2O/Na_2O$ = 61.7. The gels were vigorously stirred at 70 °C for 2 h and aged under the room temperature for 24 h, then stirred again with intermediate speed at 90 °C. After 4 h, the product was centrifugated and washed till pH 10~11. Examination with XRD, IR and SEM proved that the product was zeolite 4A.

*Keywords:* Zeolite 4A; Soft kaolin; Hydrothermal synthesis of zeolites; XRD; IR; Metakaolin

## 1. Introduction

Kaolin is one of the most versatile industrial minerals and is used extensively in many industrial applications [1]. The principal mineral in kaolin is kaolinite having a chemical formula $Al_4[Si_4O_{10}](OH)_8$ and structure consisting of a single silica tetrahedral sheet and a single alumina octahedral sheet combined to form the kaolin 1:1 layer. Soft kaolin is characterized by a smaller kaolin sand fraction. Kaolin has a wide range of applications. Owing to some special properties, such as plasticity, caking property, drying intensity, sintering character, and whiteness, kaolin is the main constituent of ceramics. Whiteness, softness, high dispersity, absorptive capacity and chemical inertness make kaolin suitable as filler in paper manufacture, rubber, and plastics. Kaolin is also used in fire retardants, in petroleum refining, in agriculture, in national defence, in cosmetic powders, in sewage purification, etc. Zeolites are porous three dimensional aluminosilicates formed by the sharing of oxygen atoms in the aluminium and silicon tetrahedral [2].

Zeolite A was first synthesized by freshly precipitated gels by Breck [3] et al. In recent years, many scholars have reported the synthesis of zeolite. Chandrasekhar [4] et al. synthesized zeolite A by the hydrothermal reaction of sodium aluminosilicate gels prepared from pure chemicals in alkaline medium using conventional heating systems. Shams [5] et al. using kaolin synthesized zeolite 5A monolith extrudates. Kaolin was heated at 800 °C for 2 h to form metakaolin. The zeolite 4A extrudate samples were converted to 5A type through ion exchange using calcium chloride solution. David [6] et al. obtained zeolite 4A from the mixture of sodium silicate, sodium aluminate, solium hydroxide, water and natural kaolin by uniform mixing. Chandrasekhar [7] et al. systematically studied the calcium exchange of kaolin based zeolites A and X. A calculated amount of sodium silicate was added to the reaction

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mixture before the hydrothermal synthesis of zeolite X. Christidis [8] et al. studied the synthetic zeolites produced from perlite waste. Zeolitisation was carried out in autoclaves with NaOH solutions at 100–140 °C. The volcanic glass was converted to zeolite-$P_c$, zeolite-V and hydroxysodalite. Marantos [9] et al. pointed that the formation of zeolite from alteration of volcanic glass is accompanied by an increase in Mg and Al content, and a decrease in Si and Na content, whereas Ca is not affected by alteration.

At present, kaolin is widely used to synthesize zeolite, because the Si/A1 ratio of the zeolite is ~1 which almost matches that of kaolin. Most scholars first convert the kaolin to metakaolin, and then the zeolite using the hydrothermal reaction. It has been reported that the yield of zeolite A produced from metakaolin is influenced by the firing temperature of the kaolin precursor [10]. Generally, a Si/Al ratio >1 in the reaction mixture is advisable for the crystallization of zeolite A and this has been achieved either by adding silica externally or by removing some aluminium from metakaolin by acid leaching or in the presence of certain Al complexing agent [11–13]. It has been observed that ancillary minerals like quartz and mica present in the kaolin remain intact during formation of metakaolin and further conversion to zeolite A [14]. However, it has been suggested that thermal pretreatment of kaolin containing quartz, in presence of sodium carbonate releases also free silica for zeolite formation and a low temperature of crystallization and dilution of alkalis facilitate formation of pure zeolite NaX [15].

Zeolite 4A has widespread applications in both laboratory and industrial scale, such as ion exchanger, molecular sieve, gas adsorbent and catalyst. For these purposes, it has been manufactured industrially on a greater scale than any other zeolite [2,16]. Kaolin is easily obtained and inexpensive, hence using kaolin to prepare zeolite 4A has significant advantages. But some problems persist (1) the calcination temperature is too high increasing production costs. Until now, metakaolin forms at temperature 550–950 °C [17]; (2) bleaching agent is needed during the calcination and crystallization so that the impurities and cost increase; (3) except for $Na_2O$ and $H_2O$, other chemical agents are needed to adjust the ratio of $SiO_2$ and $Al_2O_3$; and (4) there are few documents about using soft kaolin to synthesize zeolite.

The aim of the present work is to propose a method to produce zeolite 4A from soft kaolin. The calcination temperature is lower and other agents are not necessary except for $Na_2O$ and $H_2O$. XRD analysis has been used as the main method for identifying the phases formed during the reaction and other techniques such as Infra Red (IR) spectroscopy and scanning electron microscopy (SEM) have been used also for characterization of the end products.

## 2. Experimental

### 2.1. Raw material

The soft kaolin used in this study was obtained from Yunnan province in China. The grain size was $d_{90}$ = 17.38 μm. The chemical composition of the soft kaolin is listed in Table 1. The major constituents are $SiO_2$ and $Al_2O_3$. The concentration of other elements like sodium, potassium, iron and titanium are very low indicating the high purity of kaolin. The mineralogy studied by XRD analysis (Fig. 1a) confirms that the sample contains high amount of kaolinite and the abundance of mineral impurities is low.

Table 1
Chemical analyses of the soft kaolin

| Constituents | wt. % | Theoretical (kaolinite) |
|---|---|---|
| $SiO_2$ | 41.69 | 46.52 |
| $Al_2O_3$ | 41.18 | 39.53 |
| $Fe_2O_3$ | 0.19 | |
| $TiO_2$ | 0.13 | |
| MgO | 0.04 | |
| $K_2O$ | 0.13 | |
| $Na_2O$ | 0.18 | |
| $ZrO_2$ | 0.01 | |
| $SO_3$ | 0.15 | |
| $P_2O_5$ | 0.03 | |
| LOI | 16.25 | 13.95 |
| Si/Al ratio | 1.29 | 1.00 |

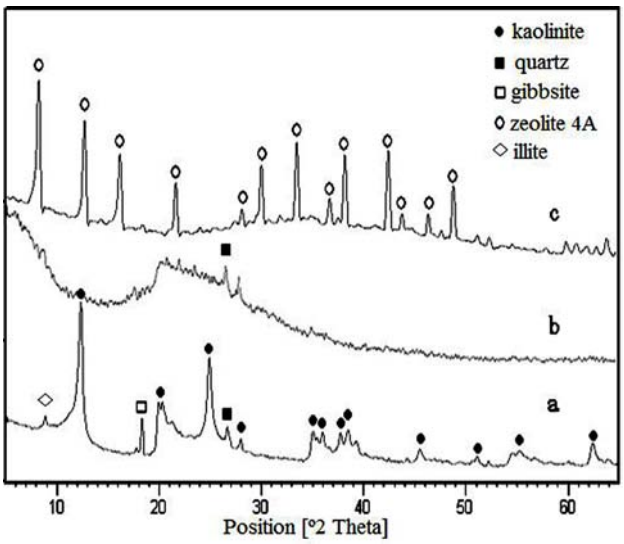


Fig. 1. XRD patterns of selected products. a-soft kaolinite, b-metakaolinite, c-zeolite 4A.

*2.2. Synthesis*

Zeolite 4A was prepared by hydrothermal synthesis. Metakaolin was obtained by heating kaolin in air at 550 °C for 2 h. A calculated amount of the metakaolin was added to an aqueous solution of sodium hydroxide, so as to keep the following molar ratios in the reaction mixture $SiO_2/Al_2O_3 = 1.7$, $Na_2O/SiO_2 = 2.8$ and $H_2O/Na_2O = 61.7$. A thorough mixing was carried out to obtain a homogeneous gel and the reactor was kept in a water bath temperature 70 °C. The mixture was vigorously stirred under uniform heating and the reactor was close to minimize evaporation loss for 2 h. And then it was aged under the room-temperature for 24 h. After ageing, the reactor was kept in the water bath at 90 °C under stirring with intermediate speed for 4 h. Subsequently the end product was centrifugated and washed untill pH 10–11. The end product was dried at 120 °C for 2 h.

*2.3. Characterization of the end product*

Chemical analysis of the end product was carried out by X-ray fluorescence spectroscopy (XRF) using a PANalytical Axios advanced XRF spectrometer (60V, 160Ma, 4KV). The particle size distribution of the sample was determined with a JI-1155 laser particle analyzer.

The mineralogical composition of the end product and the kaolin was studied by X-ray diffraction (XRD) with an X'Pert PRO Dy2198 X-ray Diffractometer using Cu Ka radiation. The phases formed were identified by comparing the d spacing and relative intensities of the samples.

IR spectra of samples were obtained with the KBr-pellet technique, by diluting 2 mg sample in 200 mg KBr. The pellets were scanned using a 370 DTGS AVATAR IR spectrometer in the range of 450~4000 $cm^{-1}$.

The morphology of the samples was examined with scanning electron microscopy (SEM) using a JSM-35CF SEM.

## 3. Results and discussion

*3.1. X-ray diffraction analysis*

XRD patterns of soft kaolinite, metakaolinite and zeolite 4A are shown in Fig. 1. The presence of amorphous matter in the XRD trace of zeolite 4A (Fig. 1c) evidenced by the hump at 25–45°, suggests that the conversion from metakaolinite to zeolite 4A was not complete.

The XRD pattern of metakaolinite is characterized by a broad hump having maximum at $2\theta \cong 22°$, indicating the presence of amorphous material, accordingly the aim of activating the soft kaolin was achieved. Quartz is also present in the metakaolin because small amounts of quartz are present in the original soft kaolin. Table 2 lists the X-ray diffraction data (d values) of zeolite 4A.

Table 2
X-ray diffraction data (d values) of zeolite 4A

| (h k l) | d Values | $I/I_{max} \times 100$ | (h k l) | d Values | $I/I_{max} \times 100$ |
|---|---|---|---|---|---|
| 1 0 0 | 12.2328 | 100 | 3 0 0 | 4.0842 | 42 |
| 1 1 0 | 8.6553 | 70 | 3 1 1 | 3.6950 | 55 |
| 1 1 1 | 7.0654 | 47 | 3 2 1 | 3.2770 | 47 |
| 2 1 0 | 5.4800 | 33 | 4 1 0 | 2.9732 | 50 |

*3.2. Infra red spectra*

The characteristic absorption bands of zeolite 4A occur at 1005 $cm^{-1}$, 660 $cm^{-1}$, 555 $cm^{-1}$ and 465 $cm^{-1}$ [18]. These bands are observed in Fig. 2, confirming the XRD results for successful synthesis of zeolite 4A.

Assignment of the IR spectral bands of zeolite 4A from soft kaolin is shown in Table 3. The characteristic bands for the vibrations due to asymmetric (at 1008.09 $cm^{-1}$) and symmetric stretch (at 665.20 $cm^{-1}$), double ring (at 554.27 $cm^{-1}$) and Si (Al)-O bends (at 459.75 $cm^{-1}$) are clearly observed in the zeolite 4A sample. The IR results thus corroborate the XRD traces of the zeolite.

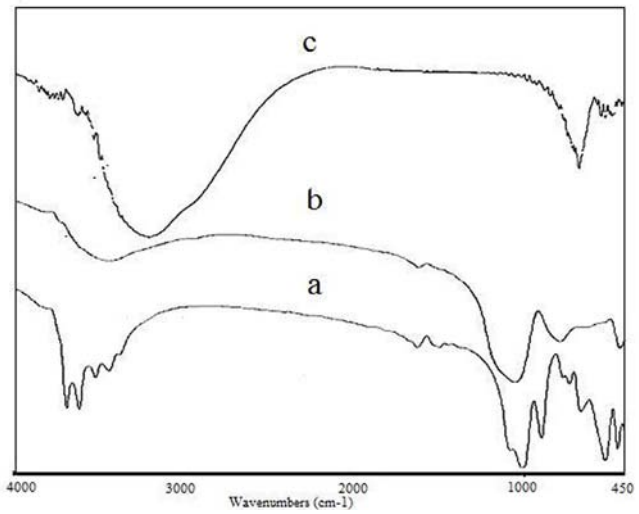


Fig. 2. IR spectra of samples. a-soft kaolin, b-metakaolin, c-zeolite 4A.

Table 3
IR spectral band assignments for zeolite 4A from soft kaolin

| Vibration frequency/$cm^{-1}$ | Attribution |
|---|---|
| 3445.12 | OH stretching vibration |
| 1650.52 | $H_2O$ offset vibration |
| 1008.09 | Asymmetry stretching vibration |
| 665.20 | Symmetry stretching vibration |
| 554.27 | Double ring vibration |
| 459.75 | Si (Al)-O flexural vibration |

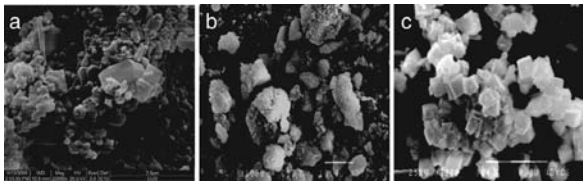


Fig. 3. SEM images of samples. a-soft kaolin, b-metakaolinite, c-zeolite 4A prepared from soft kaolin.

In Fig. 2 it can be observed that the asymmetric stretching vibration shifted from metakaolinite (at 1084.1 $cm^{-1}$) to zeolite 4A (at 1003.3 $cm^{-1}$). This can be explained as follows: when zeolite 4A was synthesized, the molecular coordination number of metakaolinite was probably adjusted in the alkaline solution and changed from octahedral to tetrahedral [19].

The characteristic bands of kaolinite (at 1075.55 $cm^{-1}$, 811.09 $cm^{-1}$, 461.31 $cm^{-1}$) are observed in Fig. 2b. The characteristic absorption bands of metakaolinite are not present in Fig. 2c, suggesting that the purity of zeolite 4A is high.

### *3.3. Scanning electron microscopic study*

Morphology of selected samples as examined under scanning electron microscope is given in Fig. 3. The soft kaolin is characterized by distorted pseudohexagonal platelets (Fig. 3a) and the metakaolin is indefinite in shape (Fig. 3b). It is obvious that the structure of kaolin has been destroyed by heating kaolin in air at 550 °C for 2.0 h. The morphology of zeolite 4A samples is shown in Fig. 3c. Zeolite 4A crystals are in the form of cubes, about 3 μm in size.

## 4. Conclusions

The soft kaolin is an excellent material for the synthesis of zeolite 4A. In this paper zeolite 4A was prepared successfully from soft kaolin without adding chemical agents. The main innovative component is the low temperature of firing for production of metakaolin, which is 550 °C instead of ~650–700 °C used by the industry. From an economic point of view, this will decrease the costs significantly.

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