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The synthesis of ZSM-5 using natural clay of Qinghai Salt Lake and its Pb(II) adsorption

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Abstract. ZSM-5 zeolite was successfully prepared through hydrothermal synthesis, for the first time, using natural clay collected from the potash ore deposit of a Salt Lake in Qaidam Basin, China. The resultant product was characterized by a series of technologies. The adsorption capacity of the final product for removing Pb (II) in aqueous solution was also investigated. The adsorption processes can be well described by the pseudo-second-order rate equation and classical Langmuir model. Results suggested that Salt Lake clay is a promising low-cost precursor for the industrial production of microporous aluminosilicate, and the ZSM-5 zeolite exhibited a potential application in Pb(II) pollution cleanup.

1 Introduction

Zeolites are crystalline microporous aluminosilicates with three-dimensional framework structure built from tetrahedral units [1]. Their specific pore sizes and large surface areas give zeolites potential applications in ion-exchangers [2], adsorbents [3], catalysts [4], removal of metal-ions from industrial wastewater [5]. The high silica zeolite ZSM-5, which was firstly reported by Mobil Co. in 1972 [6], is a medium pore zeolite formed by 10-membered rings which possesses a pore dimension of 0.54-0.56 nm. Its unique pore structure has excellent shape selectivity.

ZSM-5 is usually produced *via* a hydrothermal synthesis from a mother liquor of alkaline silicate-aluminate prepared from synthetic chemicals with organic compounds as templates. The rapid increase in consumption of zeolites calls for further work seeking cheaper raw materials for its synthesis. Efforts have been made to use mineral materials and solid wastes, such as kaolinite[7], diatomite[8], attapulgite mineral[9], gangue[10], potassium feldspar[11], fly ash [12], rice husk ash [3,13]. However, it is really difficult to remove impurities (i.e. quartz) from the raw materials. So, it is still highly required to explore new strategy for the synthesis of zeolite.

The presence of insoluble mineral components, typically clay minerals, in potash ores is a significant problem in the industry. Extensive clay accumulation occurs in low-grade sylvinitic ores, such as those mined from Salt Lakes in Qaidam Basin of Qinghai, northwestern China. Clay accumulation is a consistent concern in the potash industry and a problem that is not limited to only Qinghai potash ores. Approaches through which the clay from low-grade potash ore may be utilized have become a major consideration in potassium recovery processes.

Heavy metals are generally recognized to be a threat toward humans and ecosystems because of their high potential toxicity. Lead is a common heavy metal. Several methods have been evolved into removing Pb(II) from aqueous solution over years, One of which, adsorption method, is simple and cost-effective, thus has been widely used [14,15].



We have recently presented the direct synthesis of mesoporous aluminosilicate Al-MCM-41[16,17] and SBA-15 [18] using natural clay from low-grade potash ores of a Salt Lake in Qinghai. In this paper, we reported the synthesis of ZSM-5 zeolite from natural clay of Salt Lake via hydrothermal treatment. The method involves alkali fusion of natural clay and ZSM-5 seed. As expected, the kaolinite, illite and quartz in this natural clay could be activated completely by alkali fusion, and then hydrothermally transformed into ZSM-5 zeolite with high purity. Furthermore, the adsorption capacity of the final product obtained in this work for removing Pb(II) in aqueous solutions was also investigated.

2 Experimental

2.1 Materials

A raw representative sample of clay was collected from the potash ore deposit of a Salt Lake in Qaidam Basin, and denoted QHS. The raw QHS was crushed in a crusher. The crushed sample was thoroughly washed with distilled water to remove water-soluble components, such as K and Na, and then dried overnight at room temperature. The standard ZSM-5 zeolite was purchased from Aladdin Industrial Corporation. Sodium hydroxide was used as activating agent for QHS. The pH of gel was adjusted by hydrochloric acid. The sodium silicate was used as additional Si source. The Pb(II) solution for kinetic adsorption experiments was prepared by lead nitrate and its concentration was 25.29 mg/L.

2.2 Method

2.2.1 Alkali fusion of QHS with NaOH. NaOH and washed QHS at a 2:1 weight ratio were mixed well and fused in an MgO ceramic crucible at 500 °C for 2 h. The fused mixture was cooled to room temperature to obtain a pale and loose powder that was then used to prepare ZSM-5.

2.2.2 Preparation of aluminosilicate gel. The fused QHS powder (3.0 g) was added to distilled water (30.0 ml) with vigorous stirring for 90 minutes in a water bath at 80°C to obtain a cloudy aqueous solution with pH of 13.6. After cooling to room temperature, the supernatant was filtered to separate the solid from the liquid phase. The SiO₂/Al₂O₃ molar ratio of the clear supernatant determined by ICP-AES was 31.1, while the content of Na₂O was 57956.5 mg/L. The synthesis solution was prepared using the following composition: 154.6Na₂O: Al₂O₃: 83.4SiO₂: 4.2(TPA)₂O: 9187.8H₂O. (TPA)₂O: 9187.8H₂O. (TPA)₂O (0.2029 g) and additional Na₂SiO₃·9H₂O (2.6963g) were added to the supernatant (25 mL) with vigorous stirring until (TPA)₂O and Na₂SiO₃·9H₂O completely dissolved. The pH of the solution was adjusted to about 11.0 with 2M HCl, then white aluminosilicate gel was formed.

2.2.3 Synthesis of ZSM-5. Commercial ZSM-5 zeolite (4.5 g) was transferred with 5.0 mL distilled water to an agate mortar, and the content was grinded until colloidal liquid formed. The resultant colloidal liquid was used as ZSM-5 seed. 2-3 drops of colloidal liquid containing ZSM-5 seed were added to the above aluminosilicate gel with vigorous stirred, and the mixture was left at room temperature to aging for 48h. Then the mixture was transferred to autoclave, and crystallized at 170 °C for 72 h. After crystallization, the autoclave was carefully removed from the oven and cooled to room temperature. The white powder product in the autoclave was filtered, washed with distilled water, dried overnight at 60 °C, and calcined at 550 °C for 6 h.

2.2.4 Adsorption of Pb(II). The synthesized product ZSM-5 was used to adsorb Pb(II) in aqueous solution directly. Preliminary kinetic studies were performed at 25 °C using an initial Pb(II) concentration of 25.29 mg/L to determine adsorption equilibrium time. For this investigation, 30.0mg of calcined ZSM-5 was mixed with 40.00mL of above Pb(II) solution. The solutions were stirred in a

thermostat shaker, and fixed-volume aliquots were withdrawn at regular intervals while stirring continued. The withdrawn solution was centrifuged to separate the solid from the liquid phase. The concentration of Pb(II) in clear supernatants was determined by atomic absorption spectrometer. The adsorption quantity Q (mg/g) at time t was calculated using:

$$Q = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where C_0 and C_t are the initial and equilibrium concentrations (mg/L) of Pb(II) in solution, respectively, V is the volume (mL) of the solution, and m is the weight (g) of ZSM-5. In the sorption isotherm measurements, Pb(II) solutions (40 mL) of varying concentrations (5-80 mg/L) were agitated with ZSM-5 (30 mg) at 25 °C. After the established contact time (9 h) was reached, aliquots of the supernatant were withdrawn, and the adsorbed quantity was estimated.

2.2.5 Characterization. X-ray diffraction patterns over the 2θ range of 5° - 60° were obtained using a Rigaku D-MAX2500X diffractometer with Cu $K\alpha$ (40 kV and 200 mA). The scanning speed was $5^\circ/\text{min}$, and the step size was 0.02° . The Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer FTIR Spectrum BX-II spectrometer. Nitrogen gas adsorption-desorption isotherms were obtained at -197°C using a ASAP 2020 V3.04 H specific surface area and pore size analyzer. The concentration of Pb(II) in solution was determined by a ZEE nit700P Atomic absorption spectrometer.

3 Results and discussion

3.1 X-ray diffraction

Fig.1 shows the XRD patterns of the samples at different stages of the transformation process. The major composition of raw QHS was quartz; the remainder of the QHS was made up of kaolinite, illite and albite (Fig 1 a). These phases have low solubility and activity in the hydrothermal reaction process. Thus, before obtaining the aluminosilicate gel, QHS activation must be achieved by alkaline fusion. Based on the XRF analysis, the water-soluble aluminosilicates and sodium silicate were formed after fusing by NaOH (Fig 1b), indicating the fusion activation is effective. In addition, the adding seed is beneficial to increase the crystallization rate and improve the purity of the product. Fig 1c and 1d show the comparison of the product with a commercial zeolite ZSM-5 standard and it is apparent that the product is pure zeolite ZSM-5.

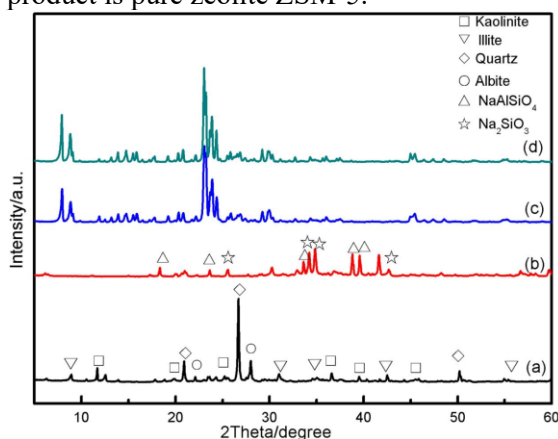


Fig 1. XRD pattern of sample:(a)the raw QHS;(b)fused QHS by NaOH;(c)product ZSM-5

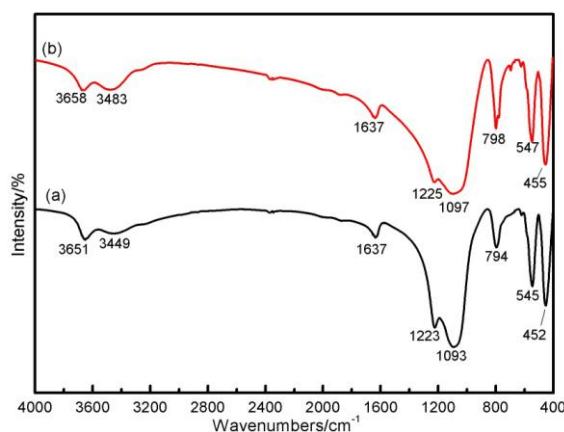


Fig.2. FTIR spectra of (a)standard ZSM-5 and (b)product ZSM-5

3.2 FTIR spectra

The FTIR spectra of the product and standard ZSM-5 were shown in Figure 2. For the synthesized product (Fig 2 b), the bands at 3658 and 1637 cm^{-1} were assigned to vibration of Si-OH on the ZSM-5 zeolite surface. The strongest vibration in the region of 1000-1250 cm^{-1} was commonly observed in (alumino) silicates due to T-O-T stretching modes, where T = Si, Al. Band at 1097 cm^{-1} was assigned to the asymmetric stretching vibrations of tetrahedral SiO_4 , while band at 798 cm^{-1} was due to symmetric stretching vibrations of the same units. The band at 547 cm^{-1} was attributed to the vibration of five- membered rings. The results were very similar to that of ZSM-5 standard or the results reported previously [3,19], which was beneficial evidence that the synthesized product was ZSM-5 zeolite.

3.3 Porosity measurements

The porosity of synthesized ZSM-5 was determined from N_2 adsorption-desorption isotherms conducted at 77 K (Fig 3). The curve exhibited a B-type loop belonged to type V isotherm with a steep step at relative pressures $p/p_0=0.4-0.5$. This indicated that the product piled into crystal plate, and opening secondary pore structure was formed in the process of stacking, which was further confirmed by the pore size distribution centered at 3.8 nm. An apparent hysteresis loop was observed in N_2 adsorption isotherm curve, which was similar to the result reported previously [20]. In addition, the BET surface area of the product ZSM-5 was $340.40\text{m}^2/\text{g}$ and its pore volume was 0.174 mL/g , similar to the conventional ZSM-5 [21].

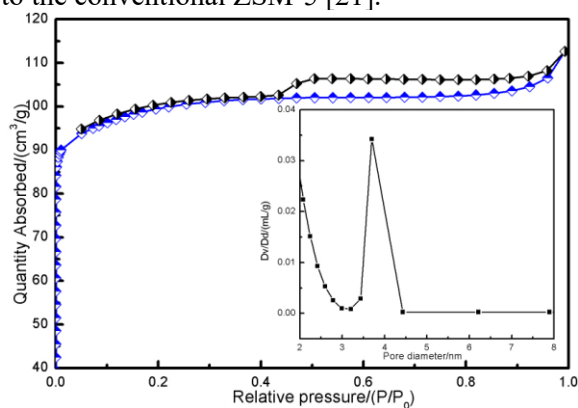


Fig 3. Nitrogen adsorption-desorption isotherms and BJH pore size distribution (inset) of calcined ZSM-5

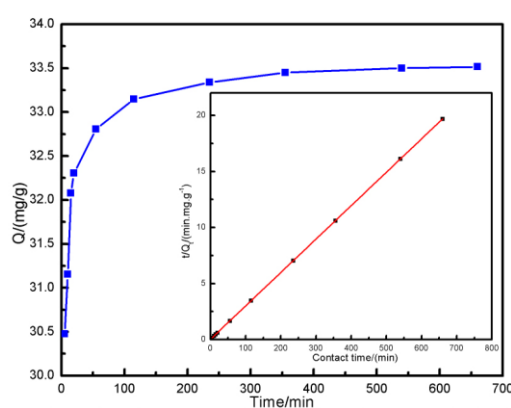


Fig 4. Time dependence of Pb(II) adsorption on synthesized ZSM-5 zeolite. $T=25^\circ\text{C}$, $C_0(\text{Pb}^{2+})=25.29\text{mg/L}$

3.4 Adsorption of Pb (II) on synthesized ZSM-5

The adsorption of Pb (II) at 25°C as a function of contact time was shown in Fig 4. The amount of Pb (II) adsorbed rapidly increased with time at the initial stages of adsorption (0-1 h range) and then gradually increased to reach equilibrium within ca. 9h under the experimental conditions. The maximum adsorption capacity of ZSM-5 for Pb(II) was 33.52 mg/g under our experimental conditions, which was comparative to those of reported previously [21]. Adsorption data were fitted by the pseudo-first and pseudo-second order kinetic model.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (2)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (3)$$

where Q_t and Q_e are the adsorption amount at time t and at equilibrium, respectively. k_1 and k_2 are the adsorption rate constant for pseudo first-and second-order models, respectively. The fitting results are given in Table 1. According to the determination coefficients, the pseudo second-order kinetic model (Fig 4, inset) provided an impressive and comparable correlation for the adsorption of Pb (II) in

contrast to the pseudo first-order model, suggesting chemical adsorption as the rate-limiting step of the adsorption mechanism and no involvement of a mass transfer in solution.

Table 1 The parameters of sorption kinetics model for Pb(II) adsorption on synthesized ZSM-5 zeolite at 25°C.

$Q_e(\text{mg/g})$	pseudo-first order kinetics			pseudo-Second order kinetics		
	$Q_{e(\text{fitted})}(\text{mg g}^{-1})$	$k_1 \times 10^2(\text{min}^{-1})$	R^2	$Q_{e(\text{fitted})}(\text{mg g}^{-1})$	$k_2 \times 10^{-2}(\text{g.mg}^{-1}.\text{min}^{-1})$	R^2
33.52	1.7045	0.90	0.9500	33.55	3.15	0.999

Preliminary thermodynamic studies were also performed at 25 °C using different concentrations of Pb (II) solution. Adsorption data were fitted by the Langmuir and Freundlich isotherm models respectively.

$$\frac{C_e}{Q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \quad (4)$$

$$\lg Q_e = \lg K_f + \frac{1}{n} \lg C_e \quad (5)$$

where b is the constant related to free energy of adsorption. K_f is the Freundlich equation constant and $1/n$ is the heterogeneity factor of the adsorbent.

Fitting parameters were listed in Table 2. According to the correlation coefficients (R^2), the Langmuir isotherm correlated better than Freundlich, suggesting a monolayer adsorption.

Table 2 Langmuir parameters and Freundlich parameters for Pb(II) adsorption on synthesized ZSM-5 zeolite at 25°C.

Ion	Langmuir model			Freundlich model		
	$Q_0(\text{mg/g})$	$b(\text{L/mg})$	R^2	n	$K_f(\text{mg/g})$	R^2
Pb(II)	46.86	3.13	0.999	4.90	25.86	0.608

4 Conclusions

The pure ZSM-5 zeolite has been successfully synthesized via hydrothermal treatment using natural clay as raw material. The alkali fusion has been demonstrated to be effective method for the activation of natural QHS clay. The product was extensively characterized, and results indicated that QHS is an appropriate precursor for synthesizing ZSM-5. The product exhibits highly thermal stability and specific surface area of 340.4 m²/g, pore volume of 0.174 mL/g, and pore size distribution centred at 3.8 nm. In addition, the result material as Pb(II) adsorbent in aqueous solution was investigated, and the adsorption amount of Pb(II) was 33.52 mg/g at 25 °C, which was comparative to the conventional ZSM-5.

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