

Manipulation of the pore size of clinoptilolite for separation of ethane from ethylene



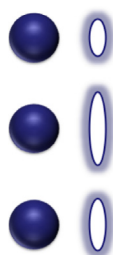
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HIGHLIGHTS

- Clinoptilolite was used and modified for ethane/ethylene separation.
- Separation performance was evaluated after ammonium exchange.
- Effect of different steaming temperatures on de-alumination and separation was studied.
- Adsorption characteristics of modified zeolite were examined.

GRAPHICAL ABSTRACT



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ARTICLE INFO

Article history:

Received 29 June 2015

Received in revised form

6 August 2015

Accepted 25 August 2015

Available online 11 September 2015

Keywords:

Clinoptilolite

Ammonium exchange

Steam treatment

Adsorptive separation

ABSTRACT

Naturally occurring zeolites are uniquely useful for small molecule separations due to the effective size of their pores. While the crystal structure of clinoptilolite has large 12-ring pores, the effective pore size of the zeolite excludes molecules larger than ~ 0.4 nm. In this work, the structure of a naturally occurring clinoptilolite was modified through ammonium exchange, calcination, and post-calcination steam treatment. The ammonium exchange removed some fraction of the structural cations, which caused the framework to expand, while steam treatment at 600 °C causes a contraction in the structure. The effective pore size of the modified clinoptilolite allowed it to adsorb ethylene and exclude ethane in a dynamic adsorption experiment. By incrementally changing the pore size of clinoptilolite, a new rate-based adsorbent for the adsorptive separation of ethylene from ethane was created.

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1. Introduction

The majority of the ethylene used in PE production is generated through the steam-cracking of ethane (Anson et al., 2008) a process which generates a mixture of ethane, ethylene, hydrogen and side products from which the ethylene must be purified. The cryogenic distillation of ethylene from ethane is energy intensive due to the two hydrocarbons similar boiling points and accounts for 25% of the production energy of ethylene (Bao et al., 2011; Ruthven, 1984; Wu et al., 2014).

Adsorptive separation of ethylene from ethane over molecular sieves offers an attractive alternative to cryogenic distillation because the separation performance is based on the strength of hydrocarbons interaction with the solid adsorbent rather than their boiling points. To achieve simultaneously high purity and high recovery of the ethylene the selectivity (defined as the preference of the molecular sieve for ethylene over ethane) must be as high as possible. Conventional zeolite molecular sieves such as 4A, 5A, 13X and CaX are equilibrium based adsorbents having a selectivity in the range 2 up to 28. While obviously ethylene selective, the modest selectivity displayed by these adsorbents will limit the performance of an adsorptive separation system due to the relatively large amount of ethane that will

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be co-adsorbed. (Jasra and Bhat, 1987; Miltenburg et al., 2006; Hosseinpour et al., 2010; Romero-Perez and Aquilar-Armenta, 2010; Mofarahi and Salehi, 2012; Narin et al., 2014).

Ethylene is nominally smaller than ethane and molecular sieves have also been developed to separate these two hydrocarbons based on their size and the associated difference in the rate in which the two gases adsorb. Pure silica Si-CHA and ITQ-3 and high silica ZSM-58 (DDR structure type) in propene/propane separation were studied. Difference of about 3 orders of magnitude adsorption rate of propene and propane exhibited by each of these zeolites while activated diffusion controlled the diffusion rate of propane (Olson et al., 2004).

In another recent study, SiCHA and DD3R, showed almost exclusive kinetic selectivity suggesting that a kinetic separation process is practically feasible and capable of yielding a high purity olefin product (Ruthven and Reyes, 2007).

AlPO-34 was used in a process for separating propylene and dimethylether from a mixture comprising propylene, dimethylether, and propane based on diffusion time constants. Dimethylether and propylene diffused at least 100 and 1000 times faster than propane, respectively, at the particular conditions of the experiment (Reyes et al., 2004a). AlPO-34 was also used in as a selective kinetic based separation to preferentially adsorb propylene from propylene/propane mixture (Reyes et al., 2004b).

The primary obstacles associated with synthesizing a size-exclusion molecular sieve is locating a zeolite having a pore diameter on the order of molecules to be separated and then finding a way to modify the pore diameter in such a way as to amplify its selectivity. Clinoptilolite is a naturally occurring zeolite having a structure containing both 8- and 10-membered rings. While it would be expected that such a zeolite would allow free access to relatively large molecules, unexpectedly, unaltered clinoptilolite will not adsorb molecules larger than 0.4 nm and, when activated, rejects both ethane and ethylene. The unexpected, ultramicroporous nature of clinoptilolite makes it an interesting potential candidate for size- or rate-based separations. This work presents the discovery that hydrothermal dealumination of calcined, ammonium-exchanged clinoptilolite effectively tunes the pore size of the zeolite. Under specific dealumination conditions ethylene can be adsorbed while ethane is effectively entirely prevented from accessing the internal surface area of the sieve under dynamic adsorption conditions.

2. Materials and methods

Naturally occurring clinoptilolite was supplied by the St. Cloud Mining Company (New Mexico, USA) with the Si/Al molar ratio of 4.13. Based on the supplier's product sheet, the clinoptilolite is at least 99% pure.

2.1. Sample preparation

Modified zeolite was prepared by exchanging 100 g of granular clinoptilolite in an ion exchange column with an ammonium chloride solution. The column was heat-traced and maintained at 80 ± 2 °C during the experiment. Based on cation exchange capacity (CEC) of 1.85 mEq/g, the granules were exchanged with an aqueous solution of 55 g of ammonium chloride dissolved in 2 L of de-ionized water. The solution was introduced at the top of the column at a constant rate of 5.5 mL/min and the flow out the bottom of the column was throttled to ensure the effluent flow rate matched the input flow rate. After ion exchange the sample was thoroughly washed, *in situ*, with de-ionized water and dried at 80 °C overnight. The dried material was spread thinly and calcined

at 5 °C/min to 500 °C in static air. The sample was maintained at 500 °C for 11 h.

Post-calcination steaming with water vapour was carried out for 2 h on 20 g samples of the rehydrated, calcined material at four different temperatures (300 °C, 400 °C, 500 °C and 600 °C) while the samples were placed in quartz tubes and heated with the heating rate of 5 °C/min to the pretreatment temperature. Nitrogen gas was humidified by passing it through an insulated glass container placed on an electric heater kept constant at 100 °C and filled with 200 mL of deionized water. The nitrogen–steam mixture was passed through the packed column at a flow rate of 30 mL/min.

3. Results and discussion

3.1. EDX

EDX result of the as-received zeolite is shown in Table 1. Calculated Si/Al ratio equals 4.13 and the level of trace impurities, as suggested by the supplier, is below 1 wt%.

3.2. XRD

Fig. 1 presents the XRD results for the as received, ion exchanged and steam treated samples. The XRD results of the as synthesized zeolite do not show any unassigned reflections other than those expected from clinoptilolite. After the various treatments the powder patterns for the treated materials were almost indistinguishable from the parent sieve, which confirms the hydrothermal stability of clinoptilolite. However, as the samples were steamed the position of the reflections moved to higher angle, indicating that the dimensions of the unit cell of the zeolite had been altered.

The contraction of the unit cell was attributed to the removal of aluminum from the framework. The average value for a tetrahedral Al–O bond is 1.74 Å, and the average value for a tetrahedral Si–O bond is 1.60 Å so as the framework aluminum is decreased, the lattice parameters are similarly expected to decrease (Kaduk and Faber, 1995). To determine the effect of dealumination the lattice parameters of the unit cell were calculated from the XRD patterns. Fig. 2 presents the value for the *a*, *b* and *c* axis respectively calculated using the Bragg equation (Breck, 1974). The (200), (020), and (002) reflections at 11.52, 12.98, and 15.52° 2θ , were used to determine the unit cell size. The pore system for clinoptilolite lies in the (110) plane so changes in the dimensions of either *a* or *b* axes would be expected to influence the pore size. Changes in the *c* direction should have no effect on the size of the pore. Fig. 2 shows that the framework did not change isotropically. The *a*-axis was more sensitive to the steaming conditions than *b*-axis and the *c*-axis and was relatively insensitive to the different treatments.

The unit cell size, as expected, did not change for the ammonium exchanged material. When steamed at 400 °C the *a*-axis showed a minor expansion while above this temperature the data shows a progressive contraction along both the *a*- and *b*-axis. Unexpectedly, the *c*-axis does not follow the same trend. The *c*-

Table 1
EDX data for the as-received natural zeolite sample.

	EDX Data								
	Na	K	Ca	Mg	Fe	Al	Ti	Si	Si/Al
(Atomic %)	0.553	0.361	0.047	0.063	0.0601	1	0.0036	4.124	4.125

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