Gas Processing Journal
Vol. 2 No. 1, January 2014
http://uijs.ui.ac.ir/gpj

Application of Zeotype SAPO-34 Molecular Sieve as a Selective Adsorbent for Separation of Ethylene from Ethane

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Abstract: The process of ethylene production from ethane dehydrogenation is one of the interesting processes in the field of conversion the petroleum light gases to the valuable products. In this process, the outlet gaseous product is a combination of ethylene, ethane and hydrogen. Effective separation techniques are required for separation of ethylene from unreacted ethane. Here a new adsorbent approach is introduced for separation of ethylene from ethane. The adsorbent is a kind of zeolite-like molecular sieve from silico-alumino-phosphate group (SAPO-34) which is previously synthesized and studied in the adsorption tests of ethane and ethylene. The equilibrium adsorption experiments are performed in a static batch adsorption apparatus at various moderate pressures and room temperature to evaluate the adsorption capacity and selectivity toward ethylene against ethane. A high tendency of SAPO-34 towards ethylene and the ethylene/ethane selectivity from 2 to 3 fold in the pressure range of 200 to 800 kPa is observed, confirming the potential application of SAPO-34 as an adsorbent in the adsorption process for separation of ethylene and ethane.

Keywords: SAPO-34, Equilibrium Adsorption, Isotherms, Selectivity, Ethylene and Ethane

1. Introduction

Light olefins are utilized as the main building blocks for many essential chemicals and products in industrial applications. Approximately, 80% of the ethylene produced in the United States and Europe is consumed in producing ethylene oxide, ethylene dichloride, and polyethylene. Ethylene oxide is the main raw material in production of surfactants, detergents, and automotive antifreeze solutions (Motelica, Bruinsma, Kreiter, den Exter, & Vente, 2012; True, 2011). For nearly seven decades, separation of olefins such as ethylene from ethane produced from dehydrogenation process are performed by a highly energy-intensive cryogenic distillation in a single or double column process with 150–200 trays at temperatures between 183 and 233 K and 1600 to 2000 kPa pressure range. The reason for the applying low temperatures and high pressures in such distillations is the similarity of boiling points of olefins and their respective paraffins. The separation process is considered to be highly heat integrated with typical ethylene refrigeration systems used for low-temperature cooling (Caballero, Grossmann, Keyvani, & Lenz, 2009; Eldridge, 1993). The high level of heat incorporation and enormous capital cost in cryogenic distillation necessitates the need for alternative separation technologies to be developed and introduce to replace the current technologies.

Any adsorption process can be proposed as a cost-effective method for such separation in a selective and efficient way at appropriate conditions. Zeolites are a kind of molecular sieves that can be proposed in separating the molecules based on their size, shape and polarity. Mofarahi and Salehi (2013)

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ISSN (On line): 2345-4172, ISSN (Print): 2322-3251

investigated pure and binary adsorption equilibrium data of ethylene and ethane on zeolite 5A with a volumetric method for the temperature range of 283 K to 323 K and the pressures up to 950 kPa. According to the experimental results, zeolite 5A has a high adsorption capacity and selectivity for ethylene in the ethylene/ethane separation system. Hosseinpour, Fatemi, Mortazavi, Gholamhoseini, and Ravanchi (2010) analyzed the adsorption behavior of methane, ethane and ethylene on 13X zeolite by equilibrium and dynamic adsorption experiments. Their results indicate that 13X zeolite would be a selective adsorbent for the separation of ethane, ethylene, and methane at moderate temperatures and pressures. Gücüyener, van den Bergh, Gascon, and Kapteijn (2010) investigated adsorption equilibrium of several mixtures on zeolite imidazolate framework ZIF-7, where ethane was selectively adsorbed and separated from ethylene. In this article, separation of ethylene from ethane by a zeolite-like molecular sieve, silicoalumino-phosphate 34 (SAPO-34), is studied and the adsorbed capacity of ethylene and ethane and selectivity of this material towards ethylene is determined against ethane. SAPO-34 is a kind of silicoalumina-phosphate with elliptical-shaped chamber (10Å×6.7Å) containing six 8-membered rings (containing eight oxygen atoms) with pore diameter of 3.8 Å which has a structure similar to Chabazite, Fig.1. Each chamber is connected to six adjacent spaces (Falconer et al., 2008). The bronsted acid sites of SAPO-34 are attributed to the introduction of Si atoms into the neutral AlPO-34 framework and SAPO-34 is a type of bronsted acid (Dai, Scheibe, Guan, Li, & Hunger, 2011; Hereijgers et al., 2009). Separation of the components from the gas mixtures are based on the difference in adsorption, penetration and screening. In the absence of specific differences between the heats of adsorption, competitive penetration is the dominant mechanism and the selectivities are the same as ideal selectivities. Whereas, in competitive adsorption the selectivity of single component will be changed due to presence of molecules that all adsorbed weakly (Caro, Noack, Kölsch, & Schäfer, 2000). Ethylene can be adsorbed most, because of its quadrapolar moment property, whereas ethane can only be adsorbed through induced polarization of ethane on the surface.

The synthesized SAPO-34 is nominated as a selective adsorbent in this study to investigation of the potential of ethylene and ethane separation (Ashraf Talesh, Fatemi, Davoodpour, & Hashemi, 2011) Although there exist some studies on other zeolites and porous materials, the equilibrium adsorption experiments are implemented for determining the adsorption capacity and selectivity of each gas in order to find out the potential of SAPO-34 for separation of ethane and ethylene from their mixtures.

2. Experiments

2.1 Materials

The procedure of SAPO-34 synthesize is derived from the previous study (Ashraf Talesh et al., 2011). This material is prepared by adopting the sol-gel hydrothermal method. The raw materials are aluminum isopropoxide, silica sol and tetra-ethyl ammonium hydroxide (TEAOH). The procedure of mixing, aging, crystallization and calcinations are similar to that of reference (Ashraf Talesh et al., 2011). The X-ray diffraction pattern of the synthesized SAPO-34 is shown in Fig.2. According to the XRD pattern, the position and the intensity of the diffraction peaks of the synthesized sample is similar to those of SAPO-34 reported in reference (Cannan et al., 1984) where there is no additional peak of impurity inside the sample. The scanning electron micrograph (SEM) of SAPO-34 is shown in Fig.3 where cube shapes of SAPO-34 crystals confirm the SAPO-34 crystal formation .

The hydrocarbons, C_2H_6 and C_2H_4 with 99.995% purity are used for adsorption experiments. Helium with 99.999% purity was used as the inert gas to measure the void volume in the adsorption experiments. Nitrogen with 99.995% purity is used for degassing and pretreatment of the adsorbent.

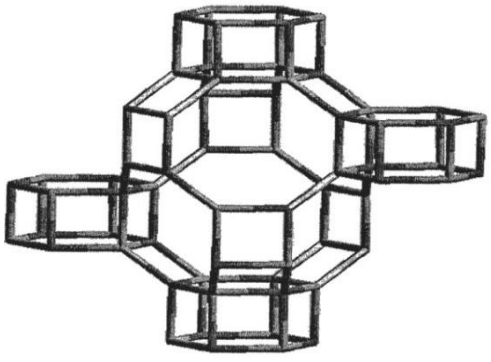

Figure 1. SAPO-34 unit structure

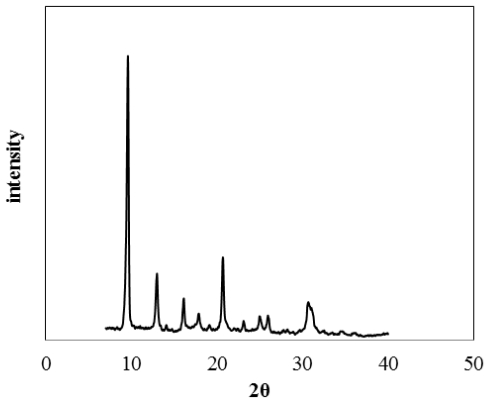

Figure 2. X-ray diffraction patterns of SAPO-34

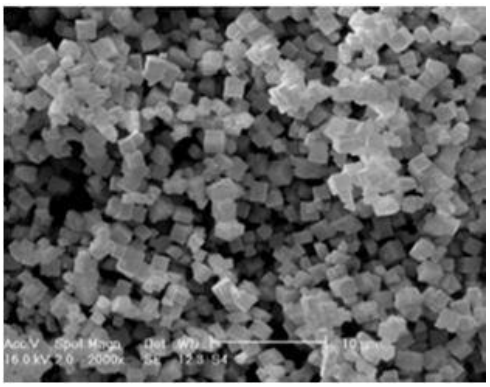

Figure 3. Image of SAPO-34 particles by scanning electron microscopy

2.2 Experimental Apparatus and Method

In this article, a high pressure system in accordance with the volumetric method is adopted to run the equilibrium adsorption tests for adsorption C_2H_4 and C_2H_6 on the SAPO-34 molecular sieve. A schematic representation of the experimental setup is depicted in Fig.4. To begin with, 5.279 gr of adsorbent is placed in the intake tank for four hours at 220°C under nitrogen stream. In order to obtain adsorption isotherms, each gas is injected in to the reference vessel in 10-1000 kPa pressure range at a constant temperature. At each one of the pressure levels, after connecting the loading cell and adsorption cell by opening the respective valve the adsorbed gas was measured by a pressure transducer. The equilibrium adsorption is achieved after a constant pressure is recorded by the pressure transducer. The experiments are implemented at other pressure levels to obtain the adsorbed amount versus any equilibrium pressure at a constant temperature, in order to sketch the isotherms. Three different isotherms are obtained by conducting the equilibrium experiments at different temperatures. For the mixture adsorption, the equilibrium adsorption is determined by the gas analysis before and after equilibrium through a GC analyzer.

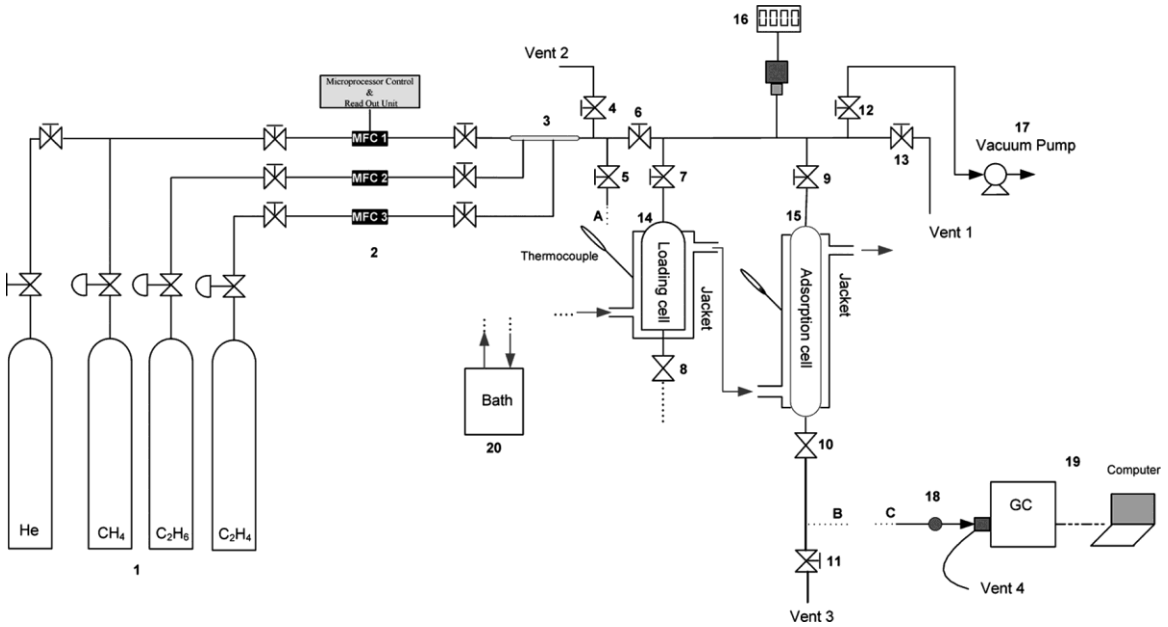

Figure 4. Adsorption apparatus; 1. Gas cylinders, 2. Mass flowmeters, 3. Mixing cell,4-13.Needlevalves, 14.Loading cell,15.Adsorption cell, 16.Pressure transducer, 17.Vacuum pump, 18.Metering valve, 19.GC analyzer,20. Circulating bath

3. Results and Discussion

3.1 Isotherms of Pure Gases

The equilibrium adsorbed of ehane and ethylene on SAPO-34 at three different temperatures are illustrated in Figures 5, 6 and 7, where the equilibrium adsorption is increased with increase in pressure at constant temperature. With a decrease in temperature the equilibrium adsorbed amount is increased; while, the kinetic rate of adsorption is decreased. It is obvious that the ethane adsorption reaches its maximum level at lower equilibrium pressure of almost 200 kPa; while, the ethylene adsorption is still increasing to the ultimate measured pressure of 900 kPa. The higher adsorption capacity of SAPO-34 towards ethylene reveals the acidity property (bronsted acid) of the adsorbent sites and attraction forces created through C=C double bond of ethylene. The lower capacity of SAPO-34 towards ethane might be attributed to the bigger kinetic diameter of ethane (0.39 nm) molecule with respect to the pore mouth size of SAPO-34 (0.38 nm). The ethane diffusion is hindered significantly in the crystal pores; therefore, the maximum adsorbed capacity achieved at lower pressures is lower. Adsorption capacity of ethane is more probable to create induced polarity through weal London forces with the surface of SAPO-34 (Prausnitz, Lichtenthaler, & De Azevedo, 1999).

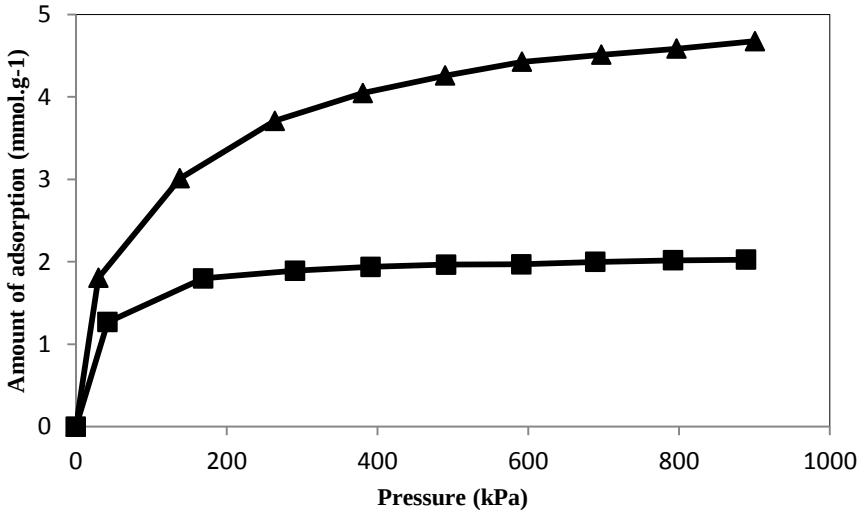

Figure 5. Single-component adsorption isotherms of C_2H_6(■) and C_2H_4(▲) on SAPO-34 at 303 K

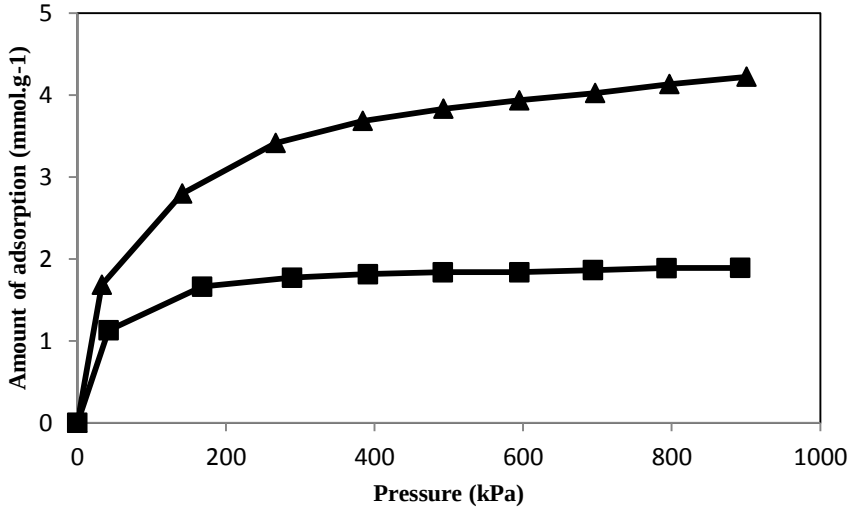

Figure 6. Single-component adsorption isotherms of C_2H_6(■) and C_2H_4(▲) on SAPO-34 at 313 K

3.2 Equilibrium Adsorption of Binary Gases

The x–y diagram, commonly used to display binary adsorption behavior, is shown in Fig.8, where the predicted adsorbed molar fraction versus gas phase composition of ethylene are shown at 600 kPa constant pressure and 303 K temperature.

In this figure it is revealed that in the mixture of ethylene-ethane, the SAPO-34 is a selective adsorbent towards ethylene. In a thermodynamic point of view ethylene-ethane separation is possible at moderate pressure and temperature. This behavior is in agreement with the ideal selectivity studies in pure component isotherms.

3.3 Selectivity

The selectivity of the adsorbent (α) for the adsorption of ethylene from an ethylene-ethane mixture at a given total pressure is calculated through:

$$\alpha_{ji} = (x_j/y_j)/(x_i/y_i) \quad (1)$$

Where, x_i, y_i are the molar fractions of ethane in the adsorbed and gas phases, respectively, and x_j, y_j are the corresponding molar fractions of ethylene.

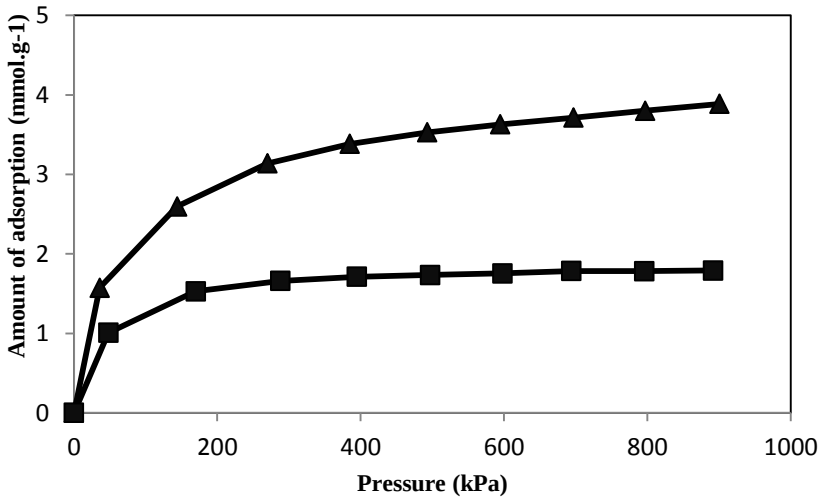

Figure 7. Single-component adsorption isotherms of C_2H_6(■) and C_2H_4(▲) on SAPO-34 at 323 K

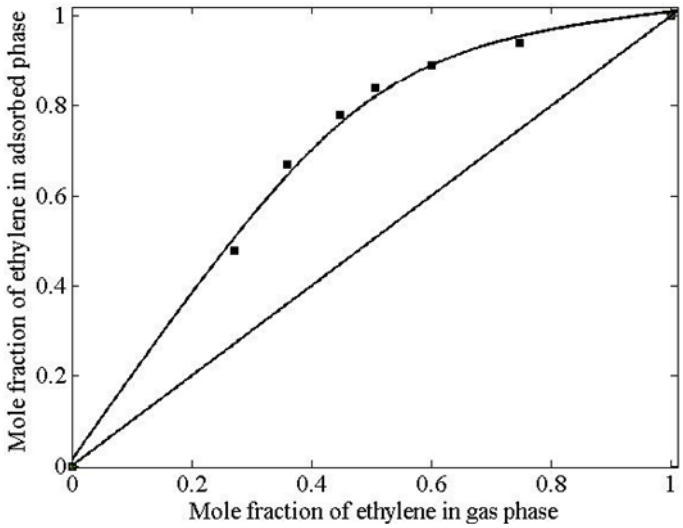

Fig. 8. Fraction of ethylene adsorbed phase versus gas phase composition at 600 kPa and 303 K

The ethylene-ethane experimental selectivity at 303 K and 600 kPa in terms of ethylene gas composition is presented in Fig.9. As can be observed, an increase in ethylene fraction of the gas phase improves the ethylene selectivity and a maximum selectivity can be observed around 0.6 mole fraction of ethylene in the mixture.

A comparison between two other types of zeolites with SAPO-34 for the ideal selectivity of C_2H_4 over C_2H_6 at various pressures is presented in Fig.10. The selectivities of 13X and 5A are lower than SAPO-34 at lower pressures, while the selectivity of SAPO-34 increases gradually as pressure is increases. Because of the larger pore sizes of both 13X and 5A than ethylene and ethane, they can diffuse through the pores and then ethylene can adsorb more strongly at lower pressures on the surface sites than ethane because of the quadrapolar properties of ethylene. By increasing the pressure, ethane forms London forces in contact to the surface and can be adsorbed on the surface; therefore the selectivity is lowered down at higher pressures. On the other hand, the smaller pore mouth of SAPO-34 hinders entering ethylene and ethane through the pore mouths at lower pressures, whereas increasing pressure causes more ethylene than ethane to get through the pores of SAPO and adsorb on the surface, therefore at higher pressures selectivity is improved. In conclusion, SAPO-34 is a better adsorbent for ethylene against ethane at higher pressures whereas 13X and 5A are preferred at lower pressures.

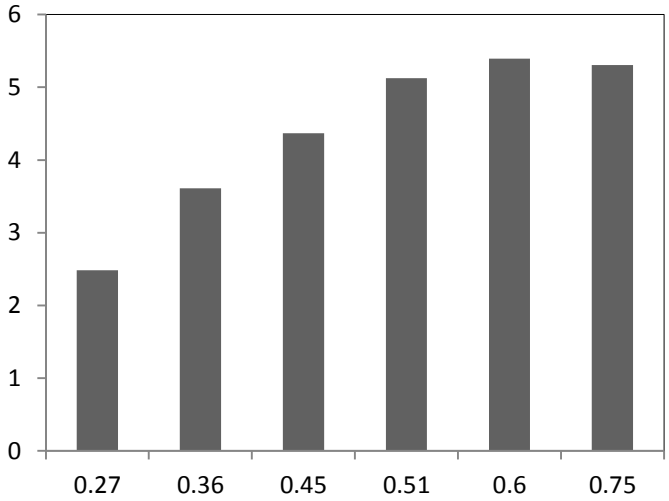

Figure 9. Selectivity of ethylene/ethane at 303 K as a function of gas composition

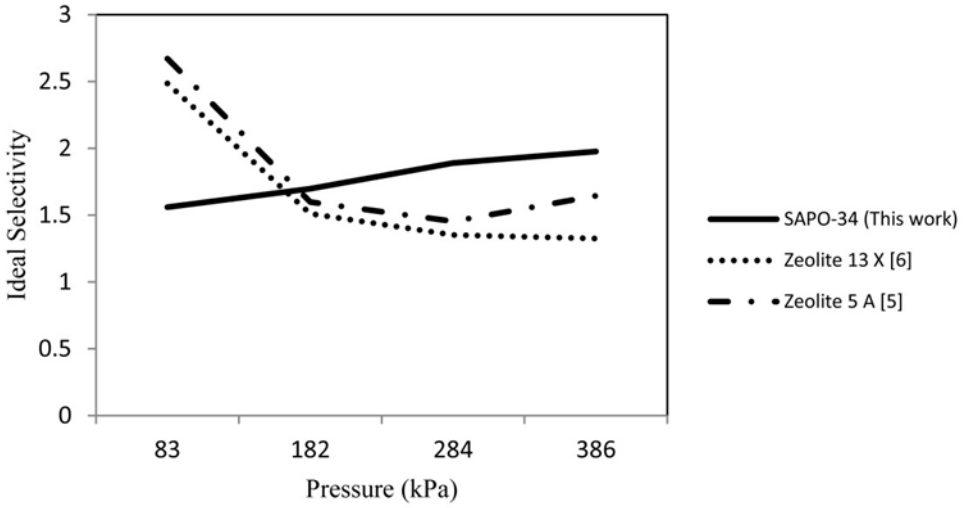

Figure 10. Selectivity of C_2H_4 against C_2H_6 and at 323K and various equilibrium pressures.
Ideal Selectivity: $(c^*_{\mu C2H4}/P_{eqC2H4})/(c^*_{\mu C2H6}/P_{eqC2H6})$

4. Conclusion

In this study, a kind of molecular sieve, the SAPO-34, is nominated for selective adsorption of C_2H_4 from C_2H_6. The adsorption isotherms of ethylene and ethane are determined in 100 to 1000 kPa pressure range and in 303 to 323 k temperature range. Ethylene/ethane selectivity is obtained from 2 to 5 fold in 200 to 800 kPa pressure range at ambient temperature. The results indicate that the potential of SAPO-34 for the selective ethylene adsorption against ethane and capability of this material in separating these gases from their mixtures at normal pressure and temperature.

Quadrapolar interactions of the molecules with double bonds greatly contribute to adsorption properties of SAPO-34 and the great difference of quadrupolar property of ethylene from ethane would be the reason for more C_2H_4 selectivity of SAPO-34. The resulted isotherms data of this work would be applicable in designing of an adsorption process for separating ethylene from ethane.

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