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Performance of CaX Zeolite for Separation of C_2H_6, C_2H_4, and CH_4 by Adsorption Process; Capacity, Selectivity, and Dynamic Adsorption Measurements

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Adsorption-based process for removal of ethane and ethylene, as the main products of oxidative coupling methane reaction from unreacted methane is discussed. The adsorption equilibrium of methane, ethane, and ethylene was determined experimentally on CaX, the calcium cation exchanged NaX zeolite, by the volumetric measurements in a high pressure setup at three different temperatures. The adsorption isotherms were well modeled by the extended Langmuir-Freundlich isotherm and the adsorbed capacity, adsorption constants, and surface heterogeneity parameter were determined by regression of the model to the isothermal experiments. The results indicated that CaX zeolite would be a selective adsorbent for the separation of ethane, ethylene, and methane from each other at moderate temperatures and pressures. The breakthrough curves of gases were determined in a dynamic adsorption experiment of the gaseous mixture in a fixed bed of CaX zeolites for a feed with similar molar composition of OCM hydrocarbon product. Significant difference of breakthrough times was observed for methane, ethane, and ethylene. It is concluded that construction of an adsorption unit from CaX zeolites at the OCM reactor downstream would be economic and useful for the separation of methane from the C_2 products.

Keywords adsorption; breakthrough curve; CaX zeolite; ethane; ethylene; methane; OCM hydrocarbons

INTRODUCTION

Of the processes for converting natural gas into a more useful chemical feedstock, the oxidative coupling of methane (OCM) has been the most intensively investigated, to form ethane and ethylene (C_2s), in recent years. The low yield of C_2 products of OCM is the main limitation of the process extension to the commercial scale. Up to date the maximum yield of C_2s is obtained 25% by the catalyst developments of OCM reaction, although this efficiency is still low and noneconomic (1). In the present work a process of adsorption is proposed for the separation of the C_2s from unreached methane. Because of the complexity of distillation and low required distilling temperature due to the low boiling point of the OCM products, adsorption is suggested as simple, high selective, and low cost method of separation (2). Many researchers have worked on different kinds of adsorbents, such as activated carbons (3–6), titanosilicates (7), zeolites, and zeolite- like materials (8–10) for the separation of light hydrocarbons. In this study, after a deep literature survey on the adsorbents and performing some prior experiments on different kinds of zeolites (11), a kind of X zeolite, calcium cation exchanged NaX, with a trade name of 10X, was prepared and examined in equilibrium and dynamic adsorption experiments for the separation of methane, ethylene, and ethane from their mixture, as the outlet hydrocarbons of OCM reaction.

The most important adsorption processes are cyclic and require adsorption-desorption step by temperature and/or pressure swing operations. Calculation of cycle time of adsorption and desorption requires knowledge of isotherm equations, capacity, and equilibrium adsorption parameters of the components. Development of the isotherm models allows prediction of the adsorption data for gaseous mixture. Adsorption equilibrium experiments provide these data for the best adsorbent selection as well as process design operational conditions. In addition to the equilibrium experiments, the dynamic adsorption experiments of the mixed gases are examined in the bed of prepared CaX zeolites to derive the breakthrough curves and breakthrough times of methane, ethane, and ethylene to get the reasonable results for possibility of efficient separation of C_2s from methane.

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EXPERIMENTAL

The experiments consist of two stages. The first part is focused on the equilibrium adsorption study of the pure gases—methane, ethane, and ethylene, to derive the capacity, selectivity, and isotherm equations on CaX zeolite. At the second stage, dynamic adsorption is considered in a packed bed of CaX zeolite at both adsorption and desorption modes for a mixture of the gases to obtain the breakthrough curves and breakthrough times of methane, ethane, and ethylene.

Materials

The gases—methane (99.995% pure), ethane (purity > 99.5%), and ethylene (purity > 99.99%) were used as the adsorbate, Helium (99.999% pure) as an inert gas for the dead volume corrections as well as the carrier gas and Nitrogen (purity > 99.99%) as a purge gas in degassing of the adsorbent was used.

NaX (or 13X) zeolite, an attrition-resistant molecular sieve (supplied by Zeochem Co. Switzerland), were used as extrudate beads with the nominal size of 1.6 to 2.6 mm. This material was cation exchanged by calcium to reduce the pore size as well as increasing the positive charge of the surface. The BET surface area was measured as 541 m^2/g with a bulk density of 650 kg/m^3. The SEM graph of the prepared CaX is observed in Fig. 1. This figure is a view of the surface with magnification of 20000. The EDAX measurements has shown substitution of calcium instead of sodium cation with molar atomic ratio of 23% Ca/(Al+Si).

Apparatus and Procedure

A two-purpose adsorption apparatus was built and set up as presented in Fig. 2 (11). At the static mode, this apparatus was used to collect the single gas adsorption equilibrium data and at the second step the system was employed for the dynamic adsorption of the mixed gases.

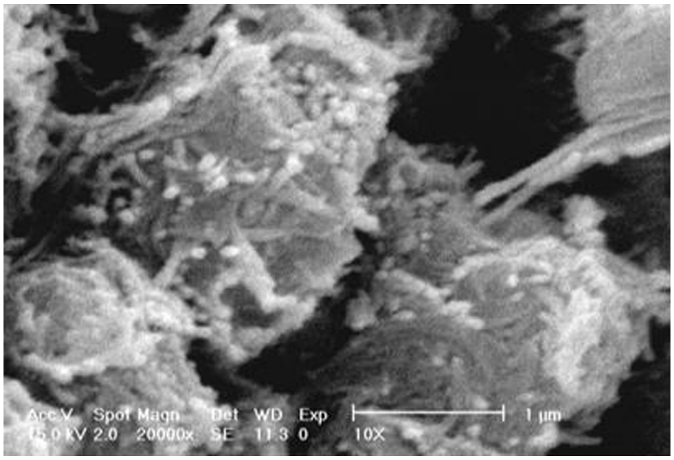


FIG. 1. SEM image of the prepared CaX zeolite.

Some of the features of this apparatus are its direct measurement of pressure at a wide range of operating conditions (pressures up to 4 MPa and temperatures up to 398 K).

There is a loading cell for collecting initial gases and an adsorption cell which allows contacting the adsorbate and adsorbent. The system can operate at two modes; static and dynamic, by closing and opening the bottom valve of the adsorption cell, respectively. For isotherm measurements of this research, two data points could be obtained during one hour.

The adsorption cell, loading cell, and dead volumes were measured using helium gas. Each cell was equipped with a thermocouple, at the center point, which operated within 0.1 K precision. The pressure was measured by a pressure transducer (ECO-1, WIKA) with an uncertainty of ±0.1% full scale. The loading cell and the adsorption cell were equipped with thermal jacket and they were maintained at a constant temperature during adsorption by a circulating bath (LCP-R133, Lab Tech).

The data collection of dynamic experiments was carried out by the GC analyzer with TCD detector on the exit gaseous stream from the bed of adsorbent.

Single Component Adsorption

The equilibrium adsorption experiments were conducted in the volumetric set up as shown in Fig. 2. The adsorption cell was filled with the weighted amount of adsorbent, with 0.001 g precision, and it was pretreated under nitrogen purge for 4 hr in 523 K followed by vacuum condition for one hour.

After setting the temperature of the loading and adsorption cell to the required level by heating /cooling jacket, the adsorption experiment was initiated by opening the valve between the loading and adsorption cell. The equilibrium state was achieved when the pressure of the system remained at a constant level for more than 30 min. The gas pressure was recorded using a pressure transducer, working with 0.01 bar precision. The experiments were conducted in various initial gas pressures from one up to 30 bars at constant temperature to derive the isotherm curve. The adsorbed amount was calculated using the difference of initial pressure and final pressure, at a constant temperature. The experiments were carried out at three different temperatures of 288, 298 and 308 K to determine the adsorption capacity of each component and selectivity of C_{2s}/CH_4, with temperature variation.

Dynamic Adsorption and Desorption

The dynamic adsorption-desorption experiments were carried out in the packed bed of CaX at normal pressure for a composition of CH_4, C_2H_6, and C_2H_4 as similar as OCM hydrocarbon products, to obtain the breakthrough curves and breakthrough times of each component. Experimental

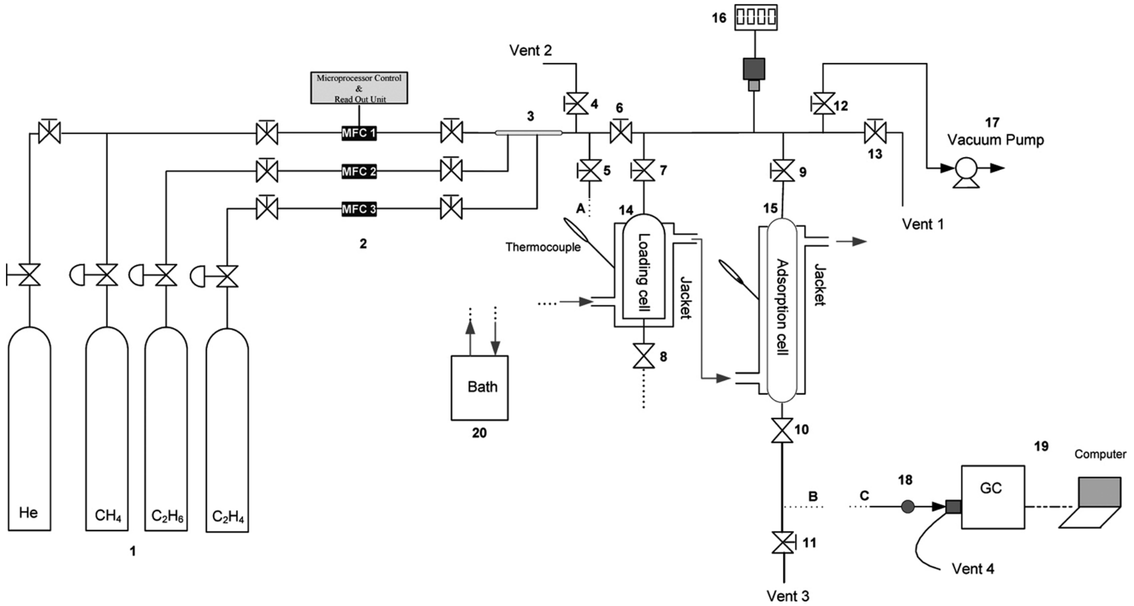


FIG. 2. Adsorption apparatus; 1. Gasses cylinders, 2. Mass flow meters, 3. Mixing cell, 4–13. Needle valves, 14. Loading cell, 15. Adsorption cell, 16. Pressure transducer, 17. Vacuum pump, 18. Metering valve, 19. GC apparatus, 20. Circulating bath.

conditions of running the dynamic adsorption and desorption experiments were tabulated in Table 1.

The schematic of Fig. 2 shows the equilibrium as well as the dynamic experimental set up. When the inlet and outlet valve of column 15 were opened and the valve of the reference cell, 14, was closed, the equilibrium system was turned off, and the dynamic method was ready to use. In this situation, feed was entered to the adsorption bed, No. 15, and the outlet gases were detected by GC at any time. This operation was continued until the outlet composition approached to the feed composition. In this way, the adsorption mode accomplished and the desorption mode was initiated by setting the temperature of the bed at the higher level, then replacing the feed with helium as the purge gas.

TABLE 1
Experimental conditions for dynamic tests

Bed properties		
	adsorbent weight	16.334 g
	inside bed diameter	1.27 cm
	bed length	20 cm
Adsorption condition		
	feed molar composition	
	CH_4	70%
	C_2H_6	15%
	C_2H_4	15%
	feed flow rate	20 N ml/min
	temperature	308 K
	pressure	Atmospheric
Desorption condition		
	helium flow rate	20 N ml/min
	temperature	323 K
	pressure	Atmospheric

ISOTHERMS MODEL

In order to have a good insight to the dynamic adsorption experiments for the mixed gases, the equilibrium adsorbed capacity and isotherm models are required to be studied. For practical utility, the experimental data should be correlated with an analytical expression that includes the temperature dependency. Various isotherm models might be tried on the experimental data, such as the Langmuir isotherm which is introduced for homogeneous systems with mono-layer adsorption. The presence of heterogeneity or/and multilayer adsorption can cause deviation of the results from the Langmuir equation.

The experimental adsorption isotherms of methane, ethane, and ethylene on CaX adsorbent were well fitted on the Langmuir–Freundlich isotherm model, as the following equation:

$$q^* = \frac{q_m b P^{(1/n)}}{1 + b P^{(1/n)}} \tag{1}$$

where q^* is the adsorbed amount at equilibrium pressure P, q_m the saturated adsorbed amount, B and n are the isotherm parameters. 'b' is the strength of the interaction between the adsorbate and the adsorbent, and '*n*' can be regarded as the parameter characterizing the system heterogeneity (12,13).

RESULTS AND DISCUSSIONS

Isotherms

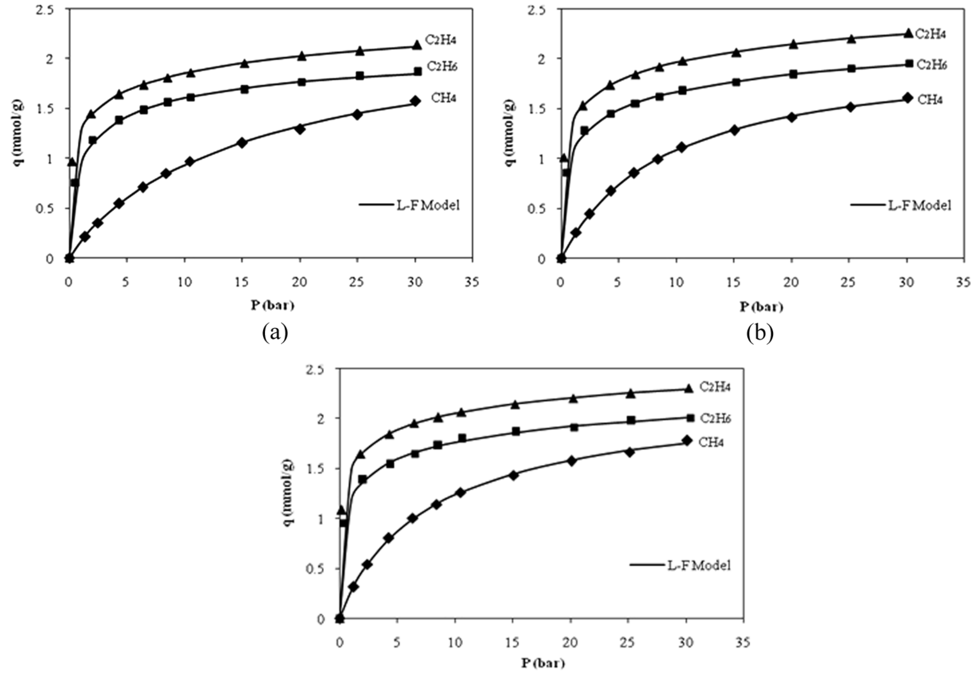
The single adsorption equilibrium isotherms of methane, ethane, and ethylene at 308, 298, and 288 K are determined from experimental results and presented in Fig. 3 (a–c), respectively. Solid lines correspond to the Langmuir-Freundlich model while dotted lines are due to the experiments. It is observed that the saturation plateau at lower temperatures is reached around lower pressures. The values of L–F parameters obtained by regression are listed in Table 2. Higher b values of ethylene suggest its strong adsorption on the CaX zeolite surface, and higher *n* value of ethylene indicates that the system of adsorbent-adsorbate is more heterogeneous than the other systems.

For all components the equilibrium adsorbed amount increased with increasing the pressure of the system although the slope decreased at higher pressures because the adsorption sites were getting close to the saturation. For all temperatures methane was weakly adsorbed relative to ethane and ethylene. Although methane, ethane, and ethylene with respectively kinetic diameters of 3.8, 4, and 3.9 Å (12,14), can diffuse through CaX zeolite pores (10 Å), the adsorbed capacity of ethylene and ethane was obtained higher than the adsorbed capacity of methane. It can be said because of the stronger attractive van-der-waals forces of C_2s with the surface, the adsorbed capacity of C_2s is more than methane. On the other hand ethylene with higher quadropole moment showed higher affinity to divalent calcium cations in CaX zeolite rather than ethane.

The L-F equation, as shown in Eq. 1 was the best fitted model on the experiments and its parameters were

TABLE 2
L-F adsorption isotherm parameters for CH_4, C_2H_6, and C_2H_4 onto CaX zeolite

T (K)	Components	q_m (mmol/gr)	b (1/bar)	n	% AARD
308	CH_4	1.985	0.073	0.904	3.21
	C_2H_6	2.290	0.691	1.886	0.960
	C_2H_4	3.340	0.619	3.274	0.420
298	CH_4	2.073	0.110	1.001	0.463
	C_2H_6	2.726	0.630	2.499	0.765
	C_2H_4	3.650	0.595	3.421	0.255
288	CH_4	2.295	0.137	1.076	1.132
	C_2H_6	2.785	0.741	2.723	0.626
	C_2H_4	3.214	0.862	3.200	0.291



(a) (b)

(c)

FIG. 3. Adsorption isotherms at three temperatures: (a) 308 K, (b) 298 K, (c) 288 K.

calculated and tabulated in Table 2 for each gas. The average absolute relative deviation (15) of experimental and fitted results was calculated using Eq. 2 and exhibited in Table 2. According to the low AARD, it is concluded that the L-F model is in agreement with experimental results.

$$AARD = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|q_i^{*Exp} - q_i^{*Mod}\right|}{q_i^{*Exp}} \tag{2}$$

According to Table 2 in each temperature, the q_m is greatest for ethylene because of the strong adsorption tendency. For methane, n is close to unity that means the L-F model of methane is getting close to the Langmuir equation. It means that methane-CaX system could be considered as a nearly homogenous system.

Selectivity of C_2s

The single component isotherm is a tool for calculating the ideal selectivity of the adsorbent for C_2s against methane. Various adsorbed amounts at different pressures and temperatures are now available from the equilibrium model to realize the ideal selectivity of ethylene and/or ethane over methane as the following formula:

$$Selectivity_{(i/CH_4)} = \frac{q_i^*}{q_{CH_4}^*} \tag{3}$$

Figure 4 exhibits the selectivity of ethane and ethylene against methane at 298 K and various equilibrium pressures, in which the results show higher selectivity of CaX towards C_2s at lower pressures, therefore atmospheric pressure was suggested for dynamic experiments because of higher separation efficiency.

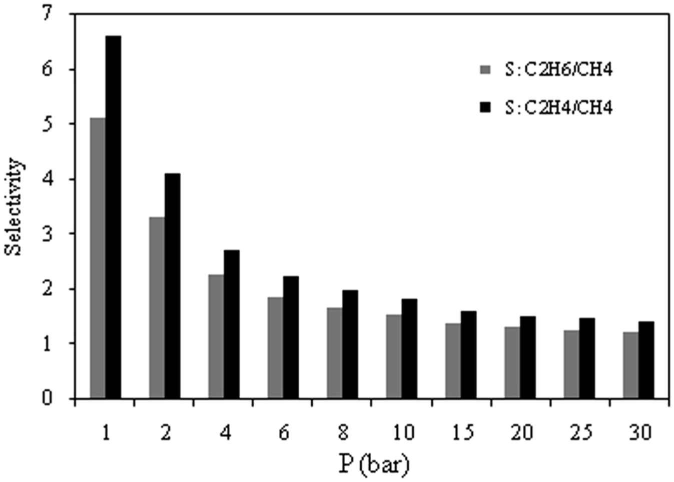


FIG. 4. Selectivities of ethane and ethylene against methane at 298 K and various equilibrium pressures.

Figure 5 reveals a comparison of the C_2s selectivities at three examined temperatures. As shown in this figure, the highest selectivity of C_2s is observed at higher temperature, 308 K. Although the adsorbed capacities are decreased at higher temperatures and require more amount of adsorbent for the dynamic process, it was proposed to work at 308 K to have higher separation efficiency of the mixed gases at dynamic conditions.

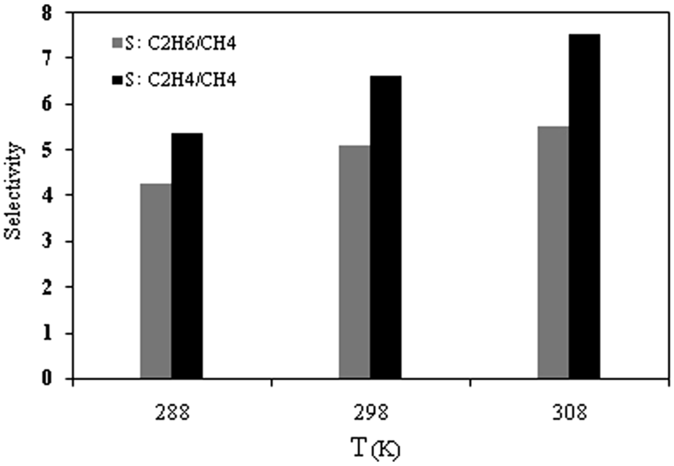


FIG. 5. Selectivities of ethane and ethylene against methane at atmospheric pressure and various temperatures.

Breakthrough Curves

The breakthrough curves of methane, ethane, and ethylene were obtained and presented in Fig. 6 as the ratio of outlet molar fraction over inlet composition. Dynamic experimental conditions were tabulated in Table 1. The results showed that methane was passed through the bulk phase at early times and appeared at the outlet stream.

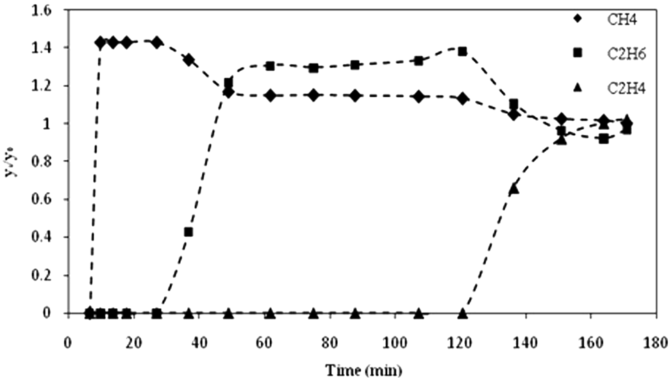


FIG. 6. Adsorption breakthrough curves of methane, ethane and ethylene on CaX zeolite at 298 K.

TABLE 3
Purity and recovery of each component in dynamic adsorption step

Comp.	Time, min	6.6		9.8	27		36.8	120.7		136.3	180.0
CH_4	Purity	0	Methane breakthrough time	100	100	Ethane breakthrough time	93.6	79.3	Ethylene breakthrough time	73.5	70.1
C_2H_6		0		0	0		6.4	20.7		16.6	14.5
C_2H_4		0		0	0		0	0		9.9	15.3
CH_4	Recovery	0		100	100		100	100		100	100
C_2H_6		0		0	0		32.7	100		100	100
C_2H_4		0		0	0		0	0		90.4	100

The breakthrough time of each component was calculated whenever 1% of inlet molar fraction appeared in the effluent and they were tabulated in Table 3. Methane breakthrough time was observed between 6.6 and 9.8 min, ethane breakthrough time was obtained from 27 to 36.8 min, and ethylene breakthrough time was observed between 120.7 and 136.3 min at dynamic adsorption processing.

Significant difference between the breakthrough times of methane and ethane shows that methane can completely exit until breakthrough time of ethane is appeared and much difference between ethane and ethylene proves a high efficient separation of ethane and ethylene from their mixture. Therefore it would be possible for methane to be separated from the products and return to the OCM reactor as the reaction feed. Table 3 has shown the purity and recovery of each gas when outgoing from the bed within each section.

After saturation of the CaX bed from the gaseous mixture, the regeneration stage was started by heating then purging by helium. The trace amount of methane remained within the bulk phase was purged at early times, then the small amount of C_2H_6 was observed in the outlet and approached to zero around 26 min, finally C_2H_4 was observed at the exit flow until 70 min. It should be noted that the bed and purge gas temperature were 323 K with 20 Nml/min flow as shown in Table 1. The desorption breakthrough curves are shown in Fig. 7 and the purity of outlet gases are calculated and shown in Table 4. It was observed that approximately after 26 min, ethylene with high purity (more than 97%) appeared at the outlet stream.

The results of adsorption and desorption stages tell us about capability of the CaX zeolite for the separation of the gases by the dynamic adsorption process, in which methane acts as a non-adsorbed material compared to ethane and ethylene, and it exits from the bed whenever ethane and ethylene are present in the feed. The desorption step tells us the possibility of regeneration of the adsorbent from the adsorbed ethylene using an inert gas such as helium or nitrogen at the higher temperatures, in this case at 323 K.

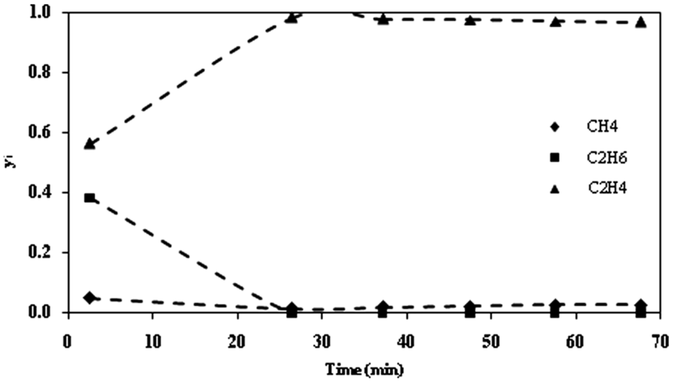


FIG. 7. Desorption breakthrough curve of methane, ethane and ethylene on CaX zeolite at 323 K.

TABLE 4
Purity of each component in dynamic desorption step

Comp.	Time, min	2.5	26.4	37.2	67.7
CH_4		5.1	1.6	2.1	3
C_2H_6	Purity	38.4	0	0	0
C_2H_4		56.5	98.4	97.9	97

CONCLUSION

CaX zeolite was prepared and examined for the separation of mixed gases of CH_4, C_2H_6 and C_2H_4, in a packed bed column at static and dynamic conditions. The static experiments were conducted for equilibrium adsorption and calculating the selectivity and isotherm parameters. Dynamic adsorption was carried out for mixed gases, similar to the composition of OCM reaction and investigated at the laboratory scale. Beakthrough curves of the gas mixture at atmospheric pressure and temperature of 308 K with 20 Nml/min flow rate over 16 g CaX zeolite showed good efficiency for the separation of methane from C_2s. The breakthrough curves at the adsorption-desorption stage were obtained to find out the breakthrough times and purity of the outlet gases. Ethylene with highly adsorption attraction on CaX zeolite was desorbed at 323 K after 70 min by the purge gas with a volume space velocity of 1 min^{-1}.

A cyclic adsorption system of TSA or PSA can be suggested for the future experiments to produce methane from the mixture at the adsorption stage and prepare ethane and ethylene at the blow down and the desorption stage.

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REFERENCES

1. Kruglov, A.V.; Bjorklund, M.C.; Carr, R.W. (1996) Optimization of the simulated countercurrent moving-bed chromatographic reactor for the oxidative coupling of methane. *Chemical Engineering Science*, 51 (11): 2945–2950.
2. Triebe, R.W.; Tezel, F.H.; Khulbe, K.C. (1996) Adsorption of methane, ethane and ethylene on molecular sieve zeolites. *Gas. Sep. Purif.*, 10 (1): 81–84.
3. Zhu, W.; Groen, J.C.; van Miltenburg, A.; Kapteijn, F.; Moulijn, J.A. (2005) Comparision of adsorption behavior of light alkanes and alkenes on Kureha activated carbon. *Carbon*, 43: 1416–1423.
4. Sung-Hyun, Kim, (2003) Adsorption equilibria of methane, ethane, ethylene, nitrogen, and hydrogen onto activated carbon. *J. Chem. Eng. Data*, 48: 603–607.
5. Esteves, Isabel A.A.C.; Lopes, Marta S.S.; Nunes, Pedro M.C.; Mota, Jose P.B. (2008) Adsorption of natural gas and biogas components on activated carbon. *Separation and Purification Technology*, 62: 281–269.
6. Siddiqi, K.S.; Thomas, W.J. (1992) The adsorption of methane-ethane mixtures on activated carbon. *Carbon*, 20 (6): 473–479.
7. Al-Baghli, Nadhir A.; Loughlin, Kevin F. (2006) Binary and ternary Adsorption of methane, ethane, and ethylene on titanosilicate ETS-10 Zeolite. *J. Chem. Eng. Data*, 51: 248–254.
8. Choudhary, V.R.; Mayadevi, S. (1993) Adsorption of methane, ethane, ethylene, and carbon dioxide on high silica pentasil zeolites and zeolite like materials using gas chromatography pulse technique. *Separation science and Technology*, 28 (13&14): 2197–2209.
9. Loughlin, K.F.; Hasanain, M.A.; Abdul-Rehman, H.B. (1990) Quaternary, ternary, binary and pure component sorption on zeolites at moderate to high pressures. *Ind. Eng. Chem. Res.*, 29: 1535–1546.
10. Choudhary, Vasant R.; Mayadevi, S. (1996) Adsorption of methan, ethane, ethylene, and carbon dioxid on silicalite-I. *Zeolites*, 17: 501–507.
11. Hosseinpoor, S. (2009) "Investigation and Application of Zeolitic Molecular sieves for separation of OCM Products," MSc thesis, Chemical Eng. Dep., Un. Tehran.
12. Anson, A.; Wang, Y.; Lin, C.C.H.; Kuznicki, T.M.; Kuznicki, S.M. (August 2008). Adsorption of ethane and ethylene on modified ETS-10. *Chemical Engineering Science*, 63 (16): 4171–4175.
13. Do, D.D. (1998) *Adsorption Analysis: Equilibria and Kinetics*; Imperial College Press: London, U.K.
14. de Vos, R.M.; Verweij (1998) Improved performance of silica membranes for gas separation. *Journal of Membrane Science*, 143: 37–51.
15. Vining, Geoffrey G. (1997) *Statistical methods for Engineers*; Duxbury press.