

# Adsorption of Propane and Propylene in Pellets and Crystals of 5A Zeolite

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Equilibrium and kinetic data for propane and propylene adsorption in pellets (Grace Davison) and crystals (PQ Corp.) of 5A zeolite are presented in the temperature range 323–423 K. The pellet adsorption loading measured by gravimetry is 1.7 mmol/g for propylene and 1.3 mmol/g for propane at 100 kPa and 423 K. The selectivity for propylene increases with temperature and is in the range 1.08–1.35 at 100 kPa, being higher at lower pressures. The kinetic data measured by zero-length-column (ZLC) chromatography indicate that the transport of sorbate in the pellets is controlled by macropore diffusion; pore diffusivities are in the range 0.018–0.027 cm<sup>2</sup>/s for both gases. Crystal diffusivities are in the range  $(1.1\text{--}7.2) \times 10^{-11}$  cm<sup>2</sup>/s for propane and  $(0.2\text{--}6.2) \times 10^{-11}$  cm<sup>2</sup>/s for propylene.

## Introduction

Adsorption techniques have been explored in the past several years as an alternative to traditional distillation processes for carrying out olefin/paraffin separations.<sup>1</sup> Propane/propylene separation is the most intensive separation performed in the petrochemical industry; polymer-grade propylene requires a purity of >99.5%. The search for an adequate adsorbent is still an important primary research activity. Adsorbents based on  $\pi$ -complexation of some metals have great potential.<sup>2,3</sup> The initial step before preparation of a “chemical adsorbent” is to know the properties of the solid matrix where the salt will be deposited, generally a commercial adsorbent.

Zeolite 5A is commonly used for the separation of iso/normal paraffins<sup>4</sup> by size exclusion. The zeolite cage of calcium zeolite 5A has an internal volume of 776 Å<sup>3</sup> formed by a cubic lattice of sodalites. The free aperture of the pore is 4.2 Å, allowing for the passage of molecules with a kinetic diameter of less than 4.9 Å.

Zeolites 13X and 4A have been extensively investigated as adsorbents for olefin/paraffin separations.<sup>5–7</sup> Zeolite 5A was also tested but not to a great extent.<sup>5</sup> The adsorption of C<sub>1</sub>–C<sub>4</sub> has been reported,<sup>8</sup> but propylene adsorption data are scarce;<sup>5,9</sup> it has been reported that coke can be formed in the adsorption process under certain conditions.<sup>10</sup>

This work was developed to investigate the possibility of using 5A zeolite commercial adsorbents as base materials for the separation of propane and propylene by the pressure swing adsorption (PSA)/vacuum swing adsorption (VSA) process. The molecular diameters of the two hydrocarbons are similar; thus, their kinetic behaviors are expected to be of the same order of magnitude (assuming macropore control with difference

only in molecular diffusion) and the separation is intended to be carried out by equilibrium (large adsorption capacity of propylene due to the double bond).

The objective of this paper is to measure adsorption equilibrium isotherms for propane and propylene in pellets and crystals of 5A zeolite by gravimetry and pore/crystal diffusivities of both species by ZLC chromatography.

## Experimental Section

The propane and propylene adsorption equilibrium isotherms presented in this work were measured in a CI–Robal microbalance (Willshire, U.K.) operated as a closed system. The activation of the sample was carried out under a vacuum at 593 K for 10 h. The heating rate to reach this temperature was 1 K/min. Isotherms were obtained at 323, 343, 373, and 423 K in the range of 0–100 kPa. All results reported were duplicated. The pressure transducer used (Lucas, U.K.) has an error of  $\pm 0.04$  kPa.

The kinetics of the two hydrocarbons was studied via zero-length-column (ZLC) chromatography. The ZLC cell was placed in a gas chromatograph oven (Carlo Erba 6000, Milan, Italy), which was also used to analyze the exit gas by flame ionization detection (FID). The dimensions of the ZLC cell used for pellet experiments, the experimental conditions, and the adsorbent properties are given in Table 1. To activate the samples (pellets and crystals), a flow of helium of 14 cm<sup>3</sup>/min at 593 K (1-K heating ramp) was used overnight (10 h at least). For crystal measurements, the cell was replaced by a stainless steel tube with two sintered filters to retain the crystals. The runs were reproducible, so we assume that no crystals passed the filters.

All gases used in this report were provided by Air Liquide: propane N35, propylene N24, and helium 50 (purities greater than 99.95, 99.4, and 99.999%, respectively). The 5A pellets were kindly provided by Grace Davison (Barcelona, Spain), and the crystals were provided by PQ Corporation (Kansas City, KS). The crystal sizes of all samples were obtained by scanning electron microscopy (SEM). The results are presented in Figure 1.

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**Table 1. ZLC Experimental Conditions and Adsorbent Properties**

ZLC characteristics (pellets)	value
cell height (cm)	1.70
cell volume (cm <sup>3</sup> )	0.27
cell porosity	0.79, <sup>a</sup> 0.94
purge flow rate (cm <sup>3</sup> /min)	34.3, 49.5, 71.0 <sup>a</sup>
pellet diameter (cm)	0.165, 0.250 <sup>a</sup>
adsorbent properties	value
pellet solid density (g/cm <sup>3</sup> )	1.74
pellet particle density (g/cm <sup>3</sup> )	1.13
pellet porosity	0.35
mean pore radius (Å)	500
crystal radius (pellets) (μm)	1.1
crystal radius (crystals) (μm)	1.0
crystal density (g/cm <sup>3</sup> )	1.57 <sup>b</sup>

<sup>a</sup> Values corresponds to experiments with large pellets. <sup>b</sup> Assumed value.<sup>9</sup>

## Theoretical Section

The selection criterion of the adsorption isotherm equation was based on the minimum number of fitting parameters including a description of the heterogeneity of the systems. The generalized Dubinin model belongs to the family of exponential isotherms that are Langmuir-nonreducible.<sup>11</sup> This model is thermodynamically incorrect because, in the low-pressure range, it does not obey Henry's law ( $q = HP$ ). However, the model contains only three parameters and can describe the behavior of a large number of systems very well.<sup>12</sup> The generalized Dubinin equation is given by

$$q = q_s \exp \left[ - \left( \frac{RT \ln \frac{P^0}{P}}{E_0} \right)^d \right] \quad (1)$$

where  $q$  and  $q_s$  are the adsorbed concentration (actual loading) and the maximum adsorbed concentration (maximum loading), respectively;  $E_0$  is the characteristic energy of adsorption; and  $d$  is the third fitting constant of the equation, which is a measure of the heterogeneity of the system.

The other model tested was the Toth isotherm.<sup>13</sup> This isotherm has been used for many systems and exhibits a great ability for fitting experimental data.<sup>14–16</sup> It is Langmuir-reducible when the heterogeneity parameter,  $n$ , is unity (homogeneous adsorbent). The other three parameters have the same physical meanings as in the Langmuir isotherm: heat of adsorption ( $\Delta H$ ), maximum adsorbed-phase concentration ( $q_s$ ), and infinite adsorption constant ( $K^0$ )

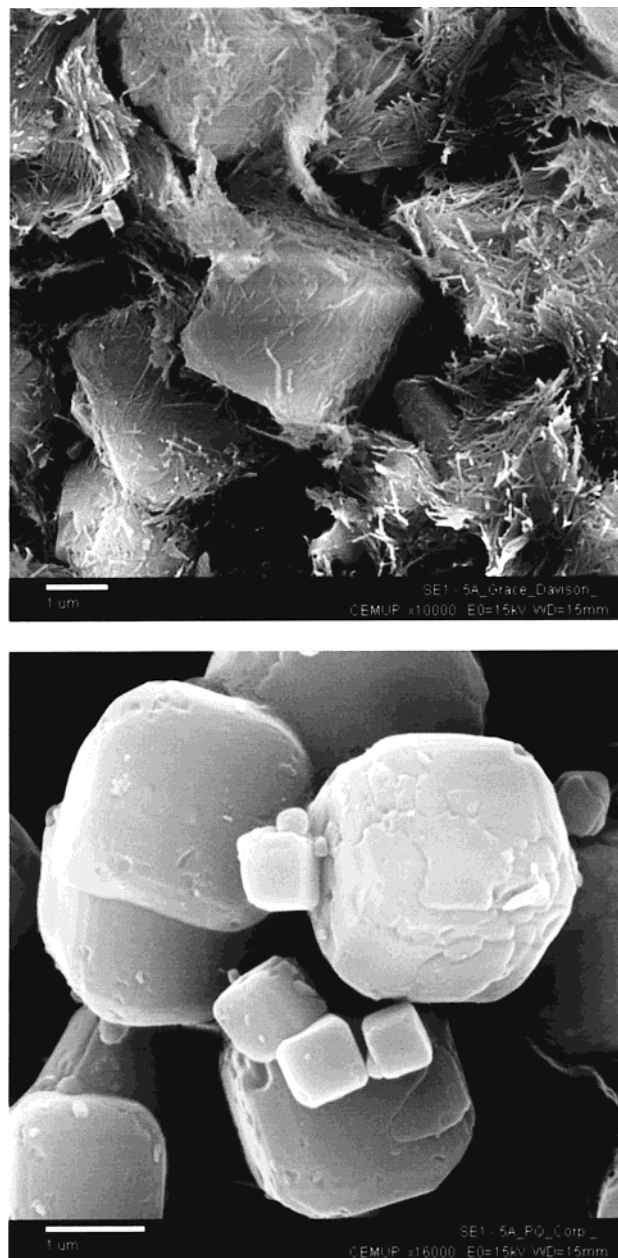
$$q = \frac{q_s (K_{eq})^{1/n} P}{(1 + K_{eq} P^n)^{1/n}} \quad (2)$$

$$K_{eq} = K^0 \exp \left( - \frac{\Delta H}{RT} \right)$$

The best-fit parameters were found by minimizing the objective function, the square of the residuals (SOR)<sup>17</sup>

$$\text{SOR (\%)} = \frac{100}{2} \sum (q_{\text{experimental}} - q_{\text{calculated}})^2 \quad (3)$$

The zero length column, ZLC, is one of the most used chromatographic methods for measuring kinetic param-



**Figure 1.** Zeolite crystals: (a) Grace Davison 5A pellets, (b) PQ Corp. crystals.

eters of a gas diffusing into an adsorbent. This method has been extensively used for crystals<sup>18–20</sup> and for pellets.<sup>15,21–22</sup> With this method, mass and heat transfer effects, together with axial dispersion, can be minimized, thus allowing for direct measurement of diffusivity parameters. The diffusivity parameters are extracted from the desorption curve of a presaturated sample purged with an inert flow. The presaturation step is generally made at low concentration (linear equilibrium zone).

ZLC analysis of macropore and micropore systems is well-documented in literature.<sup>6,23,24</sup> The special case of zeolite pellets, bidisperse adsorbents, has also been considered.<sup>25,26</sup>

In the case of spherical crystals with linear equilibrium at the surface, if the holdup in the fluid phase is neglected and perfect mixing throughout the ZLC cell is assumed, the equation that describes the changes in

the gas concentration in the desorption step is

$$\frac{C}{C_0} = 2L \sum_{n=1}^{\infty} \frac{\exp(-D_0 \beta_n^2 t / R_p^2)}{\beta_n^2 + L(L-1)} \quad (4)$$

$$\beta_n \cot(\beta_n) + L - 1 = 0 \quad (5)$$

$$L = \frac{Q_p R_c^2}{3KV_s D_c} \quad (6)$$

where  $D_c$  is the crystal diffusivity,  $Q_p$  is the purge flow rate,  $R_c$  is the crystal radius,  $V_s$  is the solid volume inside the cell,  $K$  is the Henry constant, and  $L$  is the ZLC parameter. For the case of a macroporous pellet with macropore diffusion control, similar equations can be derived

$$\frac{C}{C_0} = 2L \sum_{n=1}^{\infty} \frac{\exp(-D_{ap} \beta_n^2 t / R_c^2)}{\beta_n^2 + L(L-1)} \quad (7)$$

$$\beta_n \cot(\beta_n) + L - 1 = 0 \quad (8)$$

$$L = \frac{\epsilon_c Q_p R_p^2}{3(1 - \epsilon_p)[\epsilon_p + (1 - \epsilon_p)K]V_c D_{ap}} \quad (9)$$

where  $D_{ap}$  is the apparent diffusivity,  $\epsilon_c$  is the porosity of the cell,  $\epsilon_p$  is the porosity of the pellet, and  $V_c$  is the volume of the cell. This apparent diffusivity is expressed by

$$D_{ap} = \frac{\epsilon_p D_p}{\epsilon_p + (1 - \epsilon_p)K} \quad (10)$$

where  $D_p$ , the pore diffusivity, is related to the Knudsen and molecular diffusion by the Bosanquet equation

$$\frac{1}{D_p} = \tau_p \left( \frac{1}{D_m} + \frac{1}{D_k} \right) \quad (11)$$

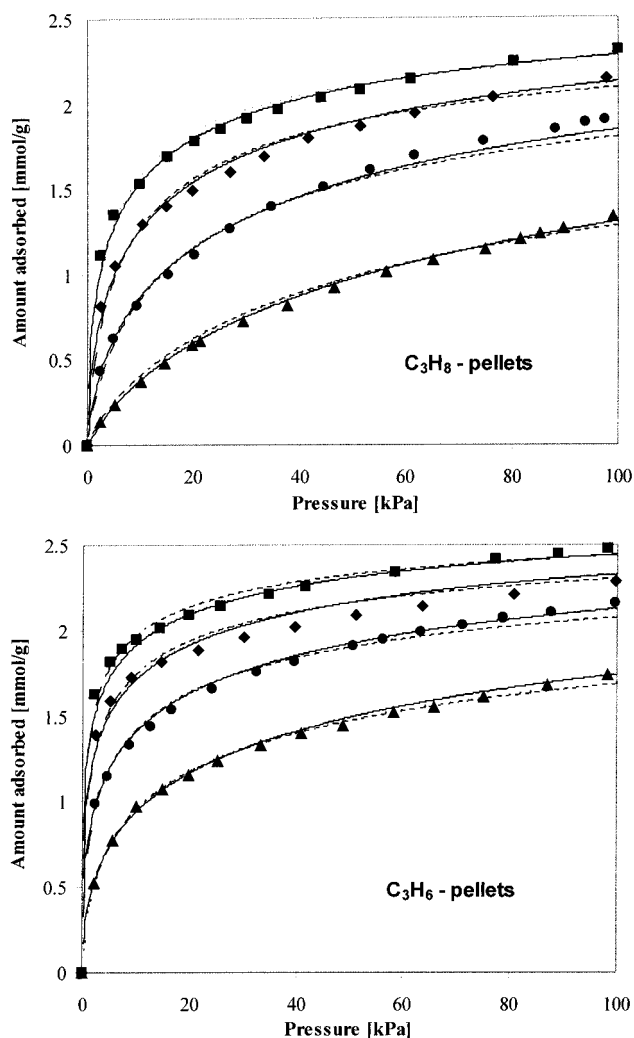
where  $D_m$  and  $D_k$  are the molecular and Knudsen diffusivities, respectively, and  $\tau_p$  is the pore tortuosity.

An alternative analysis of ZLC experiments is to use only the long-time data and thus consider only the first terms of the sums in eqs 4 and 7, which provides a simpler graphical analysis; the long-time straight line on a semilogarithmic scale is

$$\ln\left(\frac{C}{C_0}\right) = \ln\left[\frac{2L}{\beta_1^2 + L(L-1)}\right] - \frac{\beta_1^2 D_{ap} t}{R_p^2} \quad (12)$$

For the case of pellets of a bidisperse adsorbent, the simplest analysis to determine whether control is by macropore diffusion is to use pellets with different sizes. If the desorption curve is dependent on the square of the pellet size ( $R_p^2$  dependence), then the controlling mechanism is macropore diffusion; if it is independent of  $R_p$ , then the control is by crystal diffusion. In the intermediate region, the desorption curve is sensitive to the pellet size, and the controlling mechanisms are both macropore and crystal diffusion.

In this work, we measured ZLC desorption curves of propane and propylene in pellets of 5A zeolite (Grace Davison) using two pellet sizes. Desorption curves for 5A crystals (PQ Corp.) were also measured. All of the



**Figure 2.** Adsorption equilibrium isotherms in 5A zeolite pellets (Grace Davison) of (a) propane and (b) propylene. Symbols in Figure 2: ■,  $T = 323$  K; ♦,  $T = 343$  K; ●,  $T = 373$  K; ▲,  $T = 423$  K; solid lines, Dubinin model; and dashed lines, Toth model.

experiments were fitted with the complete model, eqs 4–6, and with the long time response, eqs 7–9. For the case where the complete model was used, the error function used for the minimization was the average of the residuals, ARE<sup>27</sup>

$$ARE = \frac{100}{S} \sum_{k=1}^S \left| \frac{(C/C_0)_{\text{calculated}} - (C/C_0)_{\text{experimental}}}{(C/C_0)_{\text{calculated}}} \right| \quad (13)$$

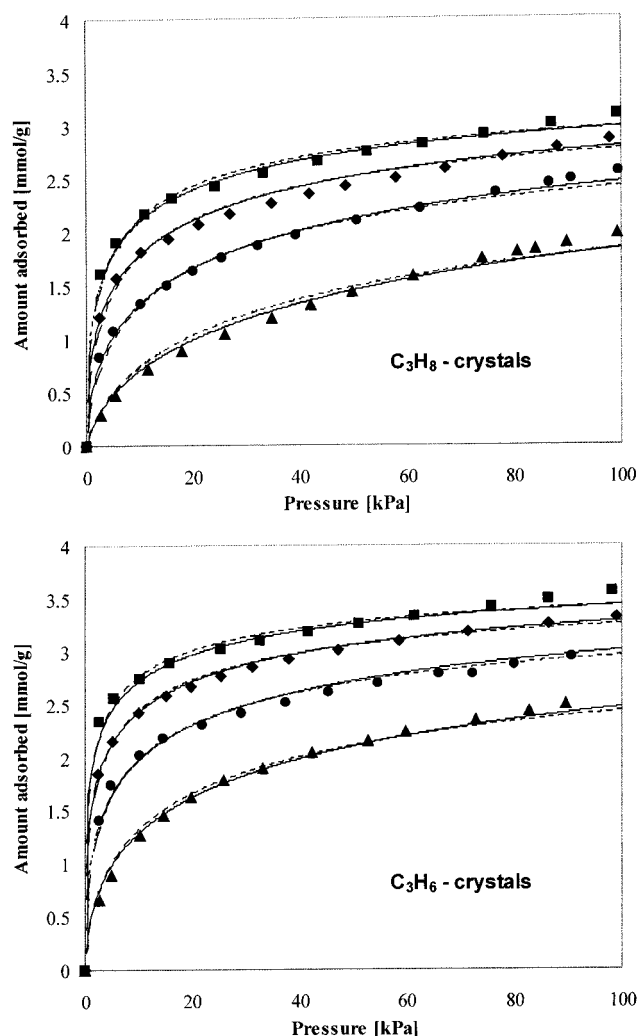
where  $S$  is the number of experimental points. If the SOR function is used in this case, the fitting will be good in the initial points (major contribution to the error) and poor in the tail of the curve. The ARE function compensate the errors in a wide range of values.

All the simulations were performed in MATLAB. The minimization routine used finds the minimum of the objective function using the Nelder–Mead simplex method of direct search.<sup>28</sup>

## Results and Discussion

The experimental adsorption equilibrium data were obtained at four different temperatures (343, 373, 423, and 473 K) for propane and propylene over zeolite 5A pellets and crystals; they are presented in Figures 2 and





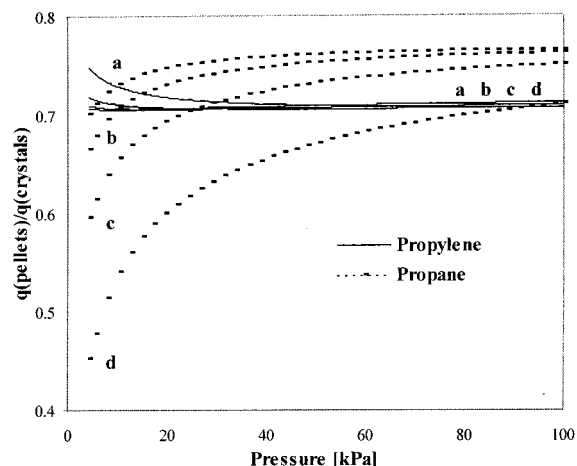
**Figure 3.** Adsorption equilibrium isotherms in 5A zeolite crystals (PQ Corp.) of (a) propane and (b) propylene. Symbols in Figure 3: ■,  $T = 323$  K; ♦,  $T = 343$  K; ●,  $T = 373$  K; ▲,  $T = 423$  K; solid lines, Dubinin model; and dashed lines, Toth model.

**Table 2. Generalized Dubinin and Toth Parameters for Propane and Propylene**

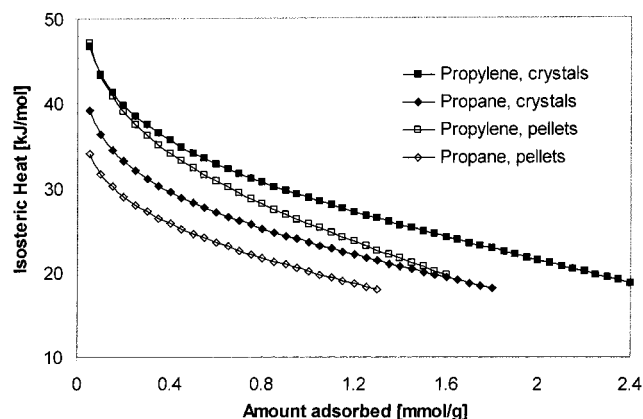
generalized Dubinin model parameters				
system	$q_s$ (mmol/g)	$E_0$ (kJ/mol)	$d$	
C <sub>3</sub> H <sub>8</sub> —crystals	3.37	19.4	2.24	
C <sub>3</sub> H <sub>6</sub> —crystals	3.75	23.4	2.28	
C <sub>3</sub> H <sub>8</sub> —pellets	2.56	18.2	2.47	
C <sub>3</sub> H <sub>6</sub> —pellets	2.71	23.4	2.13	
Toth model parameters				
system	$q_s$ (mmol/g)	$K^0$ [g/(mmol kPa)] <sup>−n</sup>	$\Delta H$ (kJ/mol)	$n$
C <sub>3</sub> H <sub>8</sub> —crystals	3.64	$4.30 \times 10^{-3}$	15.2	0.46
C <sub>3</sub> H <sub>6</sub> —crystals	4.02	$1.33 \times 10^{-2}$	14.0	0.40
C <sub>3</sub> H <sub>8</sub> —pellets	2.61	$4.94 \times 10^{-4}$	19.9	0.58
C <sub>3</sub> H <sub>6</sub> —pellets	2.93	$2.02 \times 10^{-3}$	13.4	0.36

3, respectively. In both samples, the most adsorbed gas is propylene, and all isotherms are type I (IUPAC classification) with complete reversibility. The selectivity for propylene is better at higher temperatures.

The loading in the zeolite pellets is in agreement with previous data.<sup>9</sup> In other works previously reported, the adsorption capacities of propane and propylene were lower but no indication of the amount of zeolite in the



**Figure 4.** Inert binder determination from equilibrium data: pellet/crystal loading ratio as a function of pressure: (a) 323 K, (b) 343 K, (c) 373 K, and (d) 423 K. Full lines, propylene; dashed lines, propane.



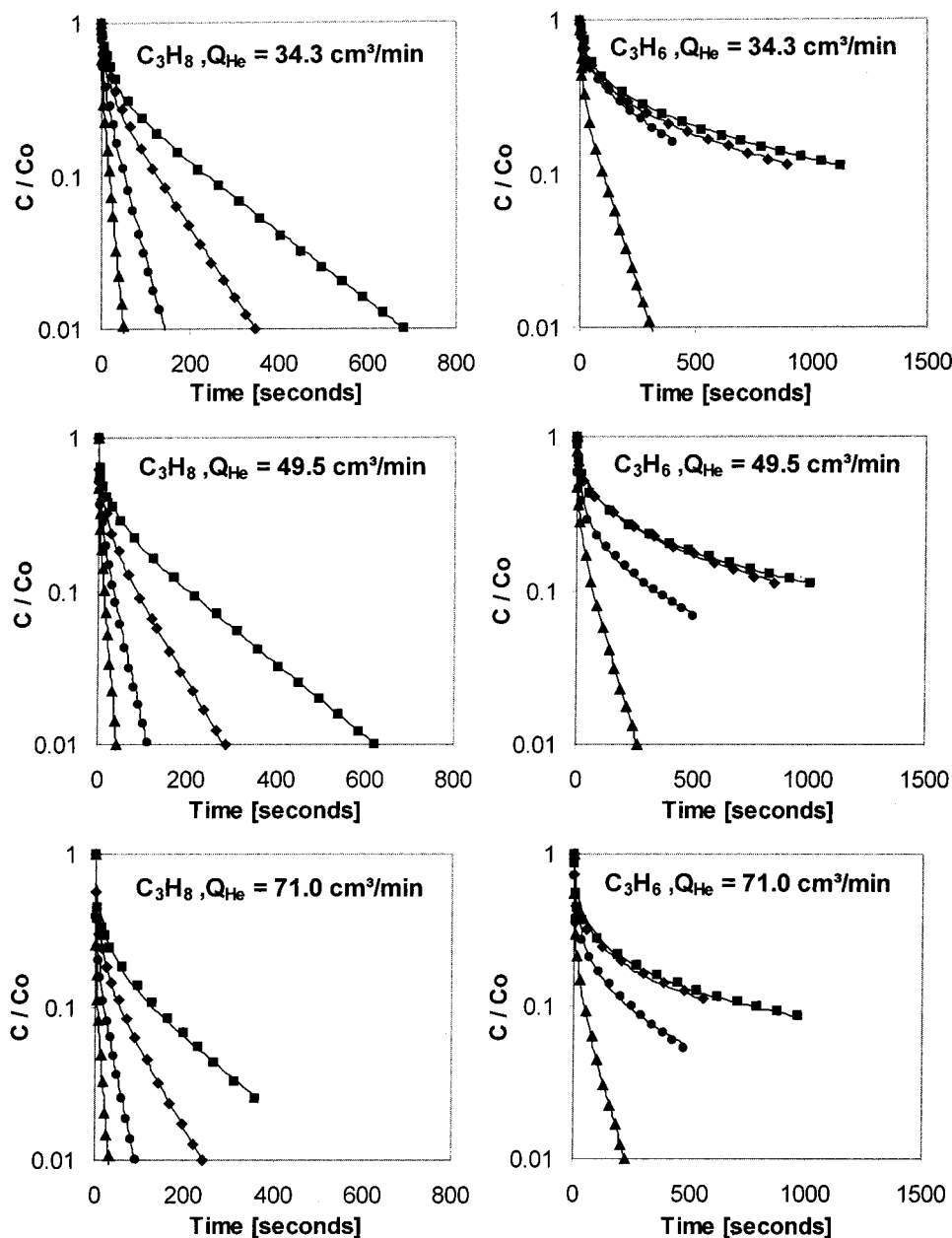
**Figure 5.** Isothermic heat as a function of amount adsorbed.

pellets was given.<sup>5,29</sup> The activation procedure could also influence the loading capacity reported in those papers.

In the figures, the dashed lines represent the Toth isotherm, and the solid lines correspond to the Dubinin model. The fitting parameters of both models are given in Table 2. The Dubinin equation fits the data very well, considering that it has only three parameters. The characteristic energies,  $E_0$ , for propane and propylene in the two samples are nearly the same, showing interactions of the same kind. The parameter  $d$  has values greater than 2 in all cases, indicating that the molecules lose at least two degrees of freedom.<sup>30</sup> Small differences in the parameter  $d$  can be attributed to fitting errors.

The fit with the Toth model also is of good quality. For this model, four constants were necessary, and the computation time was higher than that for the Dubinin isotherm. The extra computing time is due to the more difficult convergence of the simplex method resulting from the exponential description (with two parameters) of the adsorption constant. The same problem was observed in all Langmuir-reducible models. The parameter  $n$  shows the strong heterogeneity of the adsorbent, and the maximum loadings were slightly higher than predicted by the Dubinin model.

Assuming that, in both zeolites crystals (pellets from Grace Davison and crystals from PQ Corp.), the adsorption loadings are the same for propane and propylene, we calculate the amount of inert clay binder in the



**Figure 6.** ZLC desorption curves with 34.3, 49.5, and 71.0 cm<sup>3</sup>/min of He as the inert purge gas at 323, 343, 373, and 423 K in pellets of 0.165 cm. Propane (left side) and propylene (right side). Symbols in Figure 6: ■,  $T = 323$  K; ◆,  $T = 343$  K; ●,  $T = 373$  K; and ▲,  $T = 423$  K.

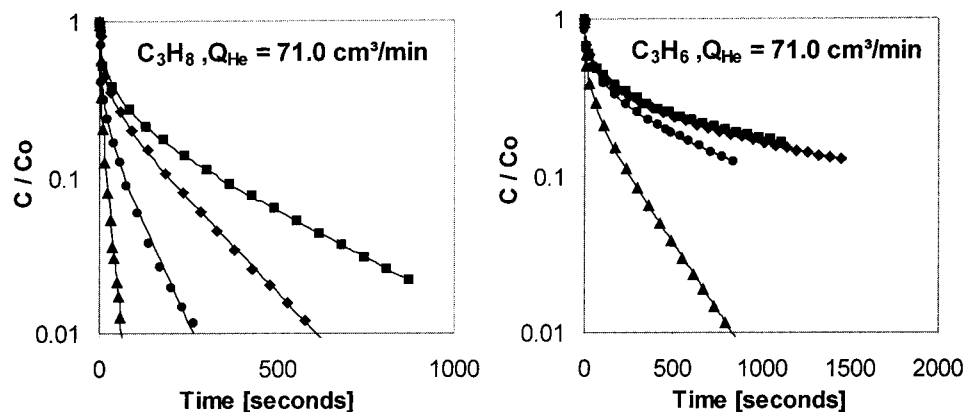
pellets. The ratios of the amounts of propane and propylene adsorbed in the pellets and crystals as functions of pressure are shown in Figure 4. The amount adsorbed on the pellets is 71% of the amount adsorbed on the crystals, indicating that the amount of inert substance is 29%.

The isosteric heat of adsorption was estimated using the Clausius–Clapeyron equation with the experimental data described by the Dubinin isotherm. The isosteric heats plotted as functions of the amount adsorbed are similar in pellets and crystals for both gases; see Figure 5.

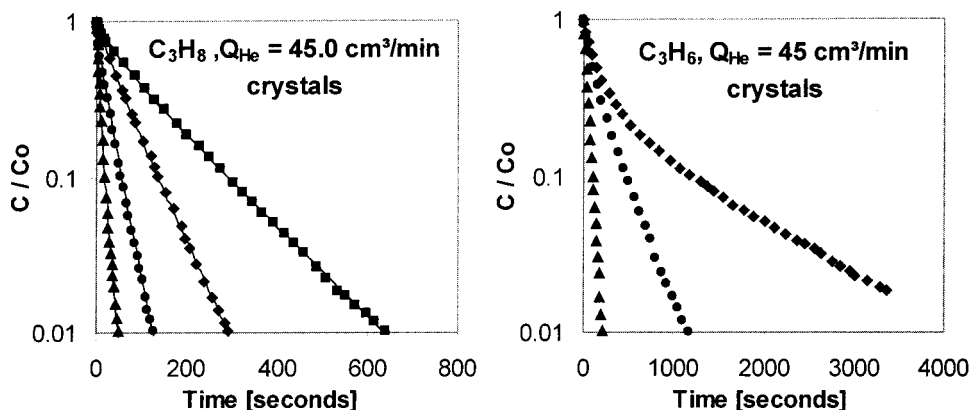
The ZLC experiments on Grace Davison 5A pellets were also carried out at 323, 343, 373, and 423 K using the three different purge flow rates of 34.3, 49.5, and 71.0 cm<sup>3</sup>/min. Two pellet sizes, 0.165 and 0.250 cm in diameter, were tested, although for one diameter (0.250-cm), the experiments were carried out only with the 71.0 cm<sup>3</sup>/min flow rate. The experiments with the PQ Corp.

crystals were carried out at 45.0 cm<sup>3</sup>/min at the same temperatures. The experimental ZLC desorption curves obtained for the pellets are presented in Figures 6 (0.165-cm pellets) and 7 (0.250-cm pellets) and for the crystals in Figure 8. The solid lines in the figures correspond to the fitting of the complete model (eqs 7–9). Additional experiments were carried out in a second cell ( $V_c = 0.06$  cm<sup>3</sup>) to determine whether the fluid phase volume influenced the results; no variations in the results were found within experimental error.

The experimental crystal diffusivity data show larger diffusivities for propane at low temperatures, but at high temperatures, the difference is not very large. The values extracted from the experiments are given in Table 3. Crystal diffusion is an activated process. In these cases, the activation energies are 8.3 and 22.4 kJ/mol for propane and propylene, respectively; the temperature dependence is plotted in Figure 9.



**Figure 7.** ZLC desorption curves with 71.0 cm<sup>3</sup>/min of He as the inert purge gas at 323, 343, 373, and 423 K in pellets of 0.250-cm diameter: (a) propane and (b) propylene. Symbols in Figure 7: ■,  $T = 323$  K; ◆,  $T = 343$  K; ●,  $T = 373$  K; and ▲,  $T = 423$  K.



**Figure 8.** ZLC desorption curves on 5A zeolite crystals (PQ Corp.) with 71.0 cm<sup>3</sup>/min of He as the inert purge gas at 323, 343, 373, and 423 K: (a) propane and (b) propylene. Symbols in Figure 8: ■,  $T = 323$  K; ◆,  $T = 343$  K; ●,  $T = 373$  K; and ▲,  $T = 423$  K.

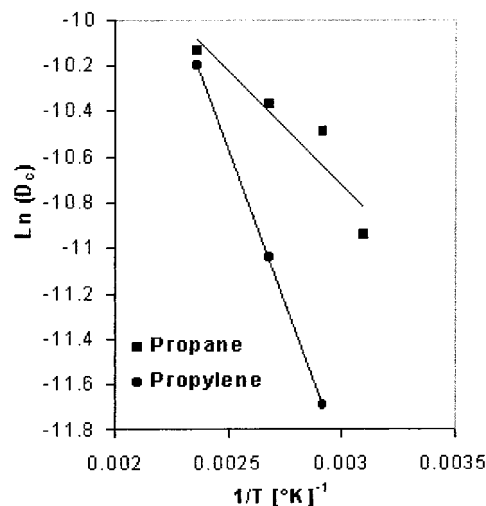
**Table 3.** Apparent Diffusivities of C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub> in 5A Zeolite Determined by ZLC<sup>a</sup>

flow rate (cm <sup>3</sup> /min)	$T = 323$ K	$T = 343$ K	$T = 373$ K	$T = 423$ K
<b>C<sub>3</sub>H<sub>8</sub> apparent diffusivity determined by ZLC</b>				
21.0 <sup>b</sup>	$5.4 \times 10^{-6}$	$1.0 \times 10^{-5}$	$2.2 \times 10^{-5}$	$5.2 \times 10^{-5}$
34.3 <sup>b</sup>	$5.2 \times 10^{-6}$	$1.1 \times 10^{-5}$	$2.7 \times 10^{-5}$	$7.3 \times 10^{-5}$
34.3	$4.4 \times 10^{-6}$	$9.7 \times 10^{-6}$	$2.3 \times 10^{-5}$	$6.3 \times 10^{-5}$
49.5	$4.9 \times 10^{-6}$	$9.3 \times 10^{-6}$	$2.4 \times 10^{-5}$	$6.0 \times 10^{-5}$
71.0	$5.1 \times 10^{-6}$	$9.5 \times 10^{-6}$	$2.5 \times 10^{-5}$	$7.1 \times 10^{-5}$
71.0 <sup>c</sup>	$5.9 \times 10^{-6}$	$1.1 \times 10^{-5}$	$2.0 \times 10^{-5}$	$8.8 \times 10^{-5}$
45.0 <sup>d</sup>	$1.1 \times 10^{-11}$	$3.2 \times 10^{-11}$	$4.2 \times 10^{-11}$	$7.2 \times 10^{-11}$
<b>C<sub>3</sub>H<sub>6</sub> apparent diffusivity determined by ZLC</b>				
21.0 <sup>b</sup>	$8.4 \times 10^{-7}$	$9.6 \times 10^{-7}$	$2.1 \times 10^{-6}$	$9.9 \times 10^{-6}$
49.5 <sup>b</sup>	$7.4 \times 10^{-7}$	$1.1 \times 10^{-6}$	$2.1 \times 10^{-6}$	$1.1 \times 10^{-5}$
34.3	$7.5 \times 10^{-7}$	$9.2 \times 10^{-7}$	$2.7 \times 10^{-6}$	$9.9 \times 10^{-6}$
49.5	$6.4 \times 10^{-7}$	$1.1 \times 10^{-6}$	$1.9 \times 10^{-6}$	$9.4 \times 10^{-6}$
71.0	$9.6 \times 10^{-7}$	$1.2 \times 10^{-6}$	$2.1 \times 10^{-6}$	$9.8 \times 10^{-6}$
71.0 <sup>c</sup>	$1.2 \times 10^{-6}$	$1.1 \times 10^{-6}$	$2.7 \times 10^{-6}$	$7.7 \times 10^{-6}$
45.0 <sup>d</sup>		$2.0 \times 10^{-12}$	$9.1 \times 10^{-12}$	$6.3 \times 10^{-11}$

<sup>a</sup> All values calculated with the long-time-response (LTR) model.

<sup>b</sup> Values obtained in the smaller cell with  $V_c = 0.06$  cm<sup>3</sup>. <sup>c</sup> Values for pellets with 0.250-cm diameter. <sup>d</sup> Values obtained with PQ Corp. crystals.

As an initial estimate, the ZLC data for the pellets were fitted with the macropore control model (eqs 7–9); if the mass transport control were intermediate (macropore and crystal) differences between the experimental and simulated results for the two pellet sizes would be significant. The values fitted with the complete-time-response (CTR) model and with the long-time-response (LTR) model are in good agreement; thus, the use of the LTR model is recommended because of its simplicity.



**Figure 9.** Temperature dependence of crystal diffusivity from ZLC curves for 5A zeolite PQ crystals.

In Table 3 we present the apparent diffusivity obtained from all of the experiments. The apparent diffusivity of propane is 6–10 times higher than that for propylene and is in the range  $(0.5\text{--}7.0) \times 10^{-5}$  cm<sup>2</sup>/s, whereas for propylene, the values are  $(0.9\text{--}9) \times 10^{-6}$  cm<sup>2</sup>/s. In all pellet calculations, the mean pore radius was used as a first estimate.

The apparent diffusivities obtained from desorption curves with the larger pellets are in agreement with the curves with smaller pellets, showing an  $R_p^2$  dependence. We can conclude that the control mechanism of mass

**Table 4. Henry's Constants, Average Pore Diffusivities, and Tortuosity Factor Estimations**

temp (K)	$K$	$D_{ap} \times 10^5$ (cm <sup>2</sup> /s)	$D_p$ (cm <sup>2</sup> /s)	$D_k$ (cm <sup>2</sup> /s)	$D_m$ (cm <sup>2</sup> /s)	$\tau$
propane						
323	2158	0.5	0.022	0.131	0.485	4.7
343	1108	1.0	0.022	0.135	0.537	4.9
373	498	2.3	0.018	0.141	0.615	6.4
423	163	7.0	0.019	0.150	0.764	6.6
propylene						
323	15912	0.1	0.026	0.135	0.535	4.1
343	12739	0.1	0.025	0.139	0.593	4.5
373	6022	0.2	0.027	0.145	0.683	4.4
423	1043	1.0	0.020	0.154	0.844	6.5

transfer in the pellets is macropore diffusion at the temperatures studied. This has also been reported for 5A sieves with diffusion measurements<sup>9</sup> from uptake experiments. Another method of determining the controlling mechanism is to calculate the ratio between the time constants for pore and crystal diffusion,<sup>26</sup>  $\gamma = (D_c/r_c^2)/(D_p/r_p^2)$ . The criterion for macropore diffusion control is  $\gamma(K+1) > 10$ . In all cases, this value was higher than 15, indicating macropore control.

In the previous literature, some differences in mass transfer control were found (macropore and micropore control).<sup>9,31</sup> These differences are explained by the use of different binders and crystal sizes.

In Table 4 are reported the average values of the pore diffusivities calculated using the Henry constants obtained from the ZLC curves. Also, with the calculated values of Knudsen and molecular diffusion, the tortuosity factors were estimated. The pore diffusivities of the two gases are very similar (0.018–0.027 cm<sup>2</sup>/s), and the average tortuosity factor estimated from 42 experiments is 5.5. This value is comparable to the values reported by Ruthven and Derrah.<sup>9</sup>

Experiments were carried out in the order 323, 343, 373, and 423 K and then repeated with the same sample. No significant changes were observed. No coke formation at higher temperatures was noticed; otherwise, in the second set of experiments, the adsorption capacity would have been lower, and the kinetic experiments would have given different results.<sup>32</sup> Also, the isotherm measurements would not be completely reversible.

## Conclusions

In this work, equilibrium (gravimetric) and kinetic (ZLC) data for propane and propylene in zeolite 5A (Grace Davison) and crystals (PQ Corp.) were measured in the 323–423 K temperature range. The selectivity of propylene at higher pressures is in the range 1.08–1.35, but at lower pressures, values higher than 2 are obtained. The zeolite content in the pellets was 71%.

The crystal diffusivity is in the range  $(1.1\text{--}7.2) \times 10^{-11}$  cm<sup>2</sup>/s for propane and  $(0.2\text{--}6.2) \times 10^{-11}$  cm<sup>2</sup>/s for propylene. The activation energies of crystal diffusion are 8.3 and 22.4 kJ/mol for propane and propylene, respectively. Mass transport in the zeolite pellets is controlled by macropore diffusion with pore diffusivities in the range of 0.018–0.027 cm<sup>2</sup>/s for both gases. This pore diffusion is mainly due to Knudsen transport. The average tortuosity factor for the Davison pellets was 5.5. The ZLC method proved to be an appropriate technique for evaluating the diffusivity parameters of these gases in zeolite 5A pellets and crystals.

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## Notation

- $C$  = molar concentration of the sorbate in the gas phase, mol/m<sup>3</sup>  
 $C_0$  = initial molar concentration of sorbate in the ZLC cell, mol/m<sup>3</sup>  
 $d$  = parameter of the generalized Dubinin model  
 $D_{ap}$  = apparent diffusivity parameter, cm<sup>2</sup>/s  
 $D_k$  = Knudsen diffusivity, cm<sup>2</sup>/s  
 $D_c$  = crystal diffusivity, cm<sup>2</sup>/s  
 $D_m$  = molecular diffusivity, cm<sup>2</sup>/s  
 $D_p$  = Pore diffusivity, cm<sup>2</sup>/s  
 $E_0$  = characteristic adsorption energy, kJ/mol  
 $K$  = Equilibrium constant  
 $K_{eq}$  = equilibrium constant from Toth model, [g/(mmol kPa)] <sup>$n$</sup>   
 $K^0$  = exponential parameter of the equilibrium constant, [g/(mmol kPa)] <sup>$n$</sup>   
 $L$  = ZLC parameter defined by eq 5  
 $n$  = heterogeneity parameter of the Toth model  
 $P$  = pressure, kPa  
 $P^0$  = pressure of the saturated gas, kPa  
 $q$  = adsorbed-phase concentration, mmol/g  
 $q_s$  = maximum adsorbed-phase concentration, mmol/g  
 $Q_p$  = purge gas flow rate, cm<sup>3</sup>/min  
 $R$  = ideal gas constant, 8.314 kJ/(mol K)  
 $R_p$  = pellet radius, cm  
 $R_c$  = crystal radius, cm  
 $S$  = number of experimental points  
 $T$  = temperature, K  
 $V_c$  = ZLC cell volume, cm<sup>3</sup>  
 $V_s$  = crystal volume inside the ZLC cell, cm<sup>3</sup>

## Greek Letters

- $\epsilon_c$  = ZLC cell void fraction  
 $\epsilon_p$  = porosity of the pellet  
 $\beta_n$  = root of elemental eq 5  
 $\beta_1$  = first root of elemental eq 5  
 $\Delta H$  = heat of adsorption (Toth model), J/mol  
 $\tau_p$  = pore tortuosity

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