

## ITQ-12: A Zeolite Having Temperature Dependent Adsorption Selectivity and Potential for Propene Separation

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A study of the adsorption properties of the new, 8-ring, pure silica zeolite ITQ-12 at several temperatures reveals that it has unique, temperature dependent adsorption selectivity and high potential for the separation of propene from propene/propane mixtures. At 30 °C, propene is adsorbed more than 100 times faster than propane, forming the basis for a kinetic based separation. Unexpectedly, at 80 °C, little or no propane adsorption is observed whereas there is no evidence for any unusual decrease in propene adsorption, a property adding to the potential of this zeolite for propene separation. A small, temperature induced decrease in the minimum dimension of the ITQ-12's "slit shaped" cages is proposed as the reason for the loss of sorption capacity for the slightly larger propane molecules. ITQ-12's unique, temperature-dependent property gives rise to a sorption selectivity that is thermodynamically driven rather than the result of diffusion barriers. Preliminary PSA simulations indicate 99.5% purity propene can be achieved with productivity significantly larger than that reported for the aluminophosphate based zeolite, AIPO-14.

### Introduction

The separation of propene from its mixtures with propane is a very important industrial process, currently performed by an energy intensive fractional distillation. An alternative process based on pressure swing adsorption would require an adsorbent with precise pore dimensions able to discriminate between these very similarly sized molecules. Recently, there have been several reports indicating the potential of 8-ring zeolites for the separation of propene from propene/propane mixtures.<sup>1–7</sup> Zhu et al. showed that propene sorbs much faster than propane in the pure silica zeolite DD3R and concluded that this zeolite could be applied to the separation of propene.<sup>1</sup> Cheng et al.<sup>2,3</sup> and Padin et al.,<sup>4</sup> from simulation and experimental studies, showed that the 8-ring aluminophosphate material AIPO-14 could separate propene from propene/propane feeds. We have shown that the pure silica zeolites Si-CHA and ITQ-3 and the high silica zeolite ZSM-58 have diffusion properties indicating that they could also achieve this separation.<sup>5,6</sup> More recently, in a preliminary communication, we reported the preparation, structure, and properties of the new, pure silica zeolite ITQ-12 (structure code ITW), and based on propene and propane adsorption rates at 30 °C, we stated it could be effective for this separation.<sup>7</sup> Herein, we report additional findings for ITQ-12, including unusual adsorption properties at moderately higher temperatures that give it further advantages and significant potential for propene separation.

### Experimental Section

The ITQ-12 zeolites used in this study were prepared as described by Boix<sup>8</sup> et al. and Barrett et al.<sup>7</sup> using fluoride, tetraethyl orthosilicate, and 1,3,4-trimethylimidazolium as structure-directing agents at 175 °C.

Adsorption measurements were made using a computer controlled thermogravimetric balance consisting of a TA51 electrobalance and associated TA-2000/PC control system. This one atmosphere, gas flow through electrobalance system was controlled via Macintosh based LabView control software, Kinetic Systems interface, mass flow controllers, and Eurotherm temperature controller. The adsorbents were activated at 500 °C for 1 h in dry nitrogen prior to the sorption measurement.  $D/r^2$  values were obtained by applying Crank's solution for diffusion in a plane sheet adsorbent.<sup>9</sup> Isotherms were fit with the Langmuir equation ( $Q = Q_{\infty}kP/(1 + kP)$ ), where  $Q$  is the weight of material adsorbed (mg/g),  $k$  is the Langmuir constant (Torr<sup>-1</sup>),  $P$  is the pressure (Torr), and  $Q_{\infty}$  is the amount adsorbed at infinite pressure. As described below, single component as well as multicomponent (sequential and competitive) adsorption measurements were performed.

Single-point adsorption capacities were computed using Accelrys Cerius<sup>2</sup> Sorption software.<sup>10</sup> This Sorption module employs a Monte Carlo method of generating possible positions for the adsorbate molecules and accepts their insertions when they are energetically favored using the pcff\_300\_1.01 force-field. Six million configurations were sufficient to achieve equilibrium. These data were used for computing the effect of decreasing the ITQ-12 cage size on adsorption properties. For these computations, we used a  $4 \times 3 \times 5$  unit cell model, i.e.,  $\sim 40 \times 45 \times 40$  Å, and an interaction cutoff of 18 Å.

Pressure swing adsorption (PSA) simulations were computed using Aspen Tech's ADSIM software.<sup>11</sup> The primary parameters used for the simulation are listed in Table 1.

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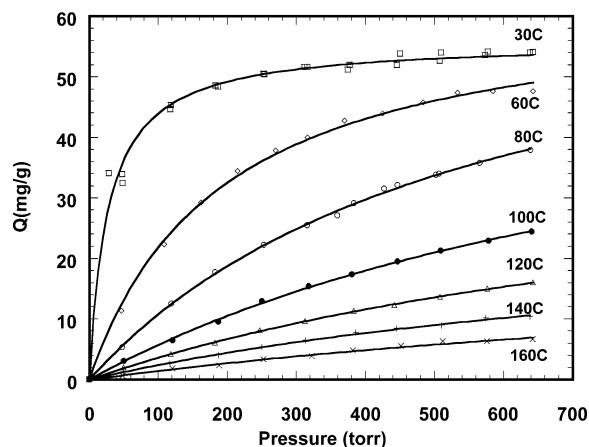
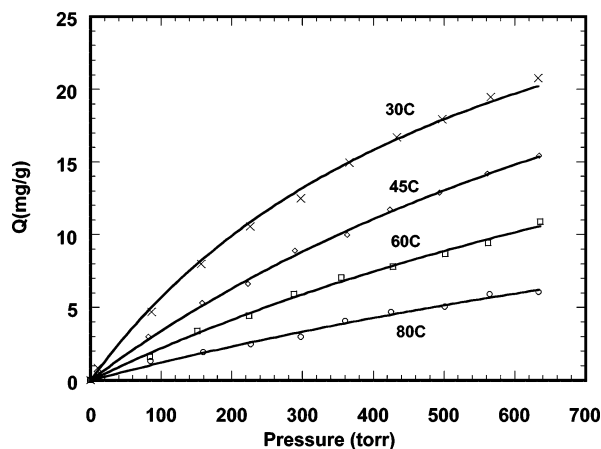
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**TABLE 1: Parameters Used for Propene/Propane PSA Separation Simulations on ITQ-12**

temperature	80 °C
pressure range	4.0 to 0.1 bar
$D/r^2$ ( $C_3^=$ )	$5.6 \times 10^{-2} \text{ s}^{-1}$
$D/r^2$ ( $C_3^o$ ) <sup>a</sup>	$2.0 \times 10^{-8} \text{ s}^{-1}$
langmuir constants	
$k(C_3^=)$	0.00177 Torr <sup>-1</sup>
$Q(C_3^=)$	56 mg/g
$k(C_3^o)$	0.0001 Torr <sup>-1</sup>
$Q(C_3^o)$	3 mg/g
bed size	1.5(h) × 0.5 (φ) m

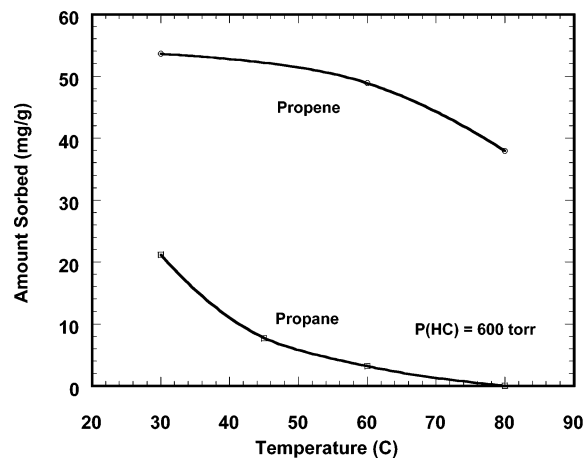
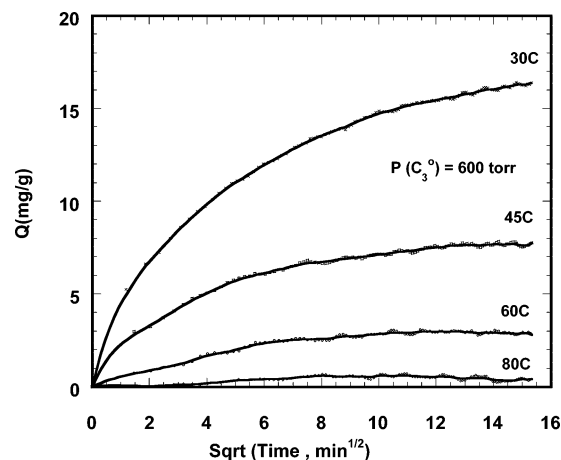
<sup>a</sup> Set arbitrarily low to ensure no adsorption of propane in accord with observations.

**Figure 1.** Propene adsorption isotherms for ITQ-12. The solid lines represent curve fitting with the Langmuir equation.**Figure 2.** Ethene adsorption isotherms for ITQ-12. The solid lines represent curve fitting with the Langmuir equation.

## Results and Discussion

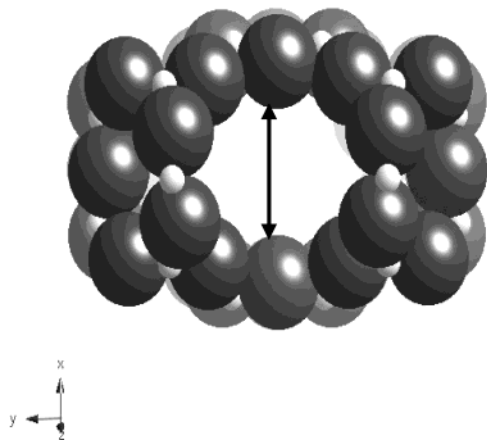
Adsorption isotherms for propene on the pure silica zeolite ITQ-12 are shown in Figure 1. The isotherms data are fitted well with the simple Langmuir relationship. The calculated isosteric heat of adsorption, 40.9 kJ/mol, is larger than the value found for Si-CHA,<sup>6</sup> 33.5 kJ/mol, consistent with ITQ-12's smaller cage size, a point to be discussed in more detail later. Similar adsorption data are shown for ethene in Figure 2; the isosteric heat is 30.5 kJ/mol compared with 27.2 kJ/mol for Si-CHA.<sup>6</sup>

Earlier, we reported that at 30 °C the rate of adsorption of propene on ITQ-12 is several thousand times faster than that for propane, indicating potential for the separation of propene from propene/propane mixtures.<sup>7</sup> Obtaining accurate values for

**Figure 3.** Effect of temperature on the sorption of propene and propane on ITQ-12 ( $P = 600$  Torr).**Figure 4.** Rate of sorption of propane in ITQ-12 at 30, 45, 60, and 80 °C.

$D/r^2$  requires knowledge of the amount of each hydrocarbon adsorbed at equilibrium, which for slowly diffusing molecules means at very long (infinite) times. Because of propane's slow sorption rate and its unexpected strong temperature dependence, obtaining reliable  $Q_\infty$  data was difficult. Previously,<sup>6</sup> we assumed that for a given temperature and pressure the number of molecules of propene and propane adsorbed per unit cell would be the same, which is the case for zeolites that have larger cages, such as Si-CHA. However, as we will show below, this is not the case for ITQ-12, for which  $Q_\infty$  for propane is much lower than for propene. The ratio of the diffusion rates of propene and propane is  $\sim 100$ .

The effect of temperature on the amount of propene adsorbed on ITQ-12, at 600 Torr, is compared in Figure 3 with values for propane. The decrease in the amount of propene sorbed with increasing temperature is as expected, with a value at 30 °C of 54 mg/g, dropping to 38 mg/g at 80 °C. The results for propane are surprising. The amount sorbed at 30 °C,  $\sim 22$  mg/g, is much lower than the 54 mg/g found for propene and drops to  $\sim 0$  mg/g at 80 °C. We must point out that, since the adsorption rates for propene are fast, the values shown in Figure 3 represent equilibrium, whereas because the rate of adsorption of propane is much slower, there is uncertainty in its  $Q_\infty$  values. The adsorption of propane in ITQ-12 at 30, 45, 60, and 80 °C is shown in Figure 4. The curves are nearly horizontal at 240 min adsorption time indicating that these values are not far from equilibrium. These pseudo limiting values are used in Figure 3. The correctness of these values should increase with



**Figure 5.** Space filling model of the cage in ITQ-12 (front atoms removed) viewed along the [001] diffusion pathway. The free distance between four-ring oxygen atoms is  $\sim 3.9$  Å. Large and small spheres represent O and Si atoms, respectively.

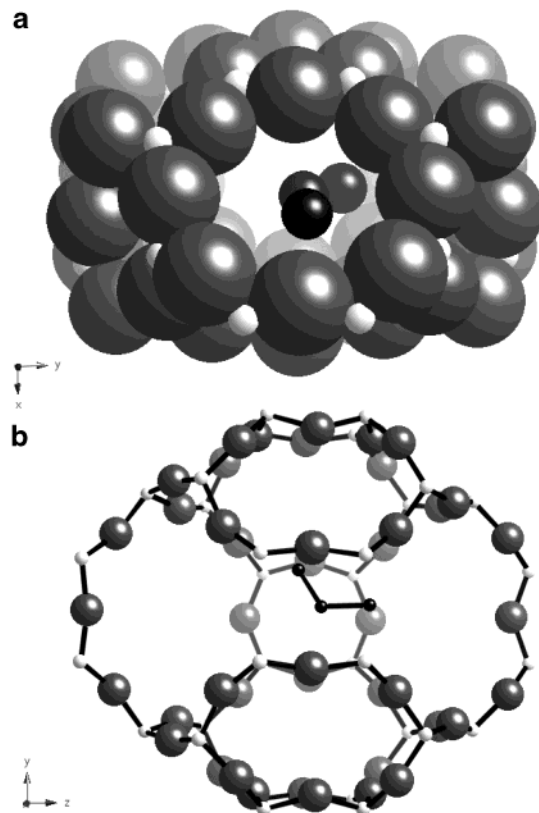
increasing temperature since with increasing temperature the rate of approach to equilibrium increases for an activated diffusion process.

We hypothesize that this unexpected adsorption behavior is due to thermodynamic and not kinetic factors. The following discussion supports this hypothesis, and empirical observations also supporting this view will be detailed at the end of the next section.

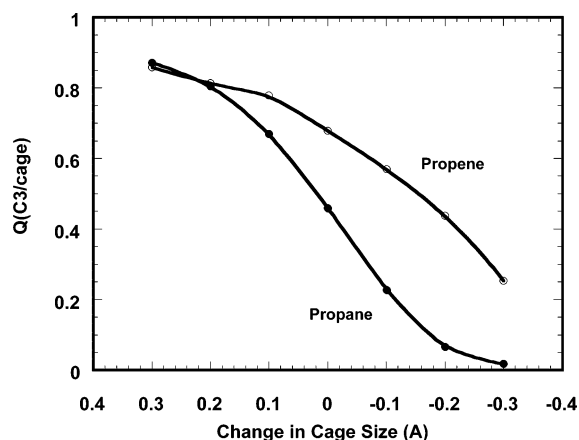
Diffusion in the channel system of ITQ-12 is in the [001] direction and limited by eight-rings having dimension of  $3.9 \times 4.1$  Å.<sup>7</sup> The  $\sim 3.9$  Å minimum dimension of the eight-rings creates a barrier for the diffusion of propane (Figure 5). In many high silica, eight-ring zeolites, the energy barrier for passage of propane through eight-rings is frequently in the 70–90 kJ/mol range.<sup>6,12</sup> ter-Horst et al. have attributed this high barrier primarily to changes in the C–C–C bond angle, computed to be  $\sim 12^\circ$ , as the propane molecule passes through the eight-ring zeolite.<sup>12</sup> Little bond angle change is required for the propene molecule for this translation. The other eight-ring in ITQ-12 is too small for the passage of hydrocarbon molecules ( $2.4 \times 5.3$  Å).<sup>7</sup>

ITQ-12's primary pore volume is defined by small, 32 T-atom,  $[4^5 5^4 6^4 8^4]$  cages, shown in Figure 5. Having dimensions of  $3.9 \times 8.5 \times 9.6$  Å, the cage interior resembles a narrow slit (Figure 6, parts a and b). The cages are interconnected via the  $3.9 \times 4.1$  Å eight rings.

Because of the constraints on the propane, and propene molecules, as they pass through the eight rings, “in the ring” is not an equilibrium position for either of these molecules but rather the ring is the main barrier to diffusion. Indeed, a structure analysis of propene loaded ITQ-12 reveals one molecule of propane per cage, located in the center of the cage (Figure 6, parts a and b) with its C–C–C plane parallel to the plane of the cage slit.<sup>13</sup> The minimum dimension of the cage, 3.9 Å, may be somewhat smaller than the optimum size for maximum propane adsorption and thus any decrease in size would bring greater repulsive forces into play. We have attempted to model this effect by artificially increasing and decreasing the minimum [100] cage dimension by moving the four four-ring oxygen atoms, on one side of the cage, in steps of  $-0.3$ ,  $-0.2$ ,  $-0.1$ ,  $0$ ,  $0.1$ ,  $0.2$ , and  $0.3$  Å followed by simulation<sup>10</sup> of the equilibrium amount sorbed, separately, for propene and propane at 80 °C and 600 Torr (Figure 7). For the reference structure, the calculated sorption is 0.45 and 0.68 molecules/cage of propane and propene, respectively. In qualitative agreement with the

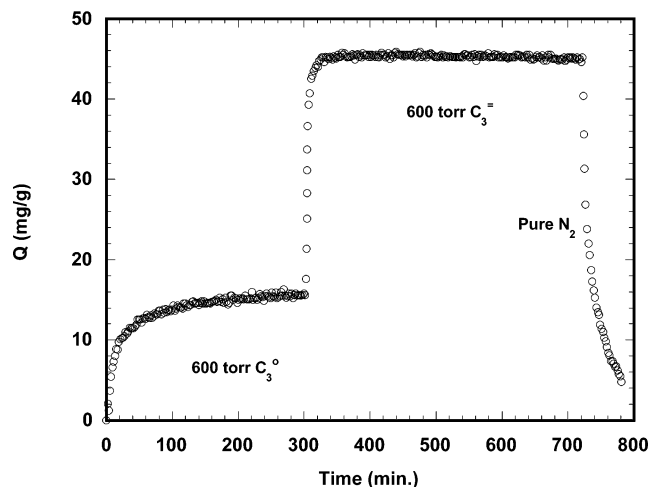


**Figure 6.** (a) Space filling model of the propene in the cage in ITQ-12 (front atoms removed) viewed along the [001] diffusion pathway. Large, medium and small spheres represent O, C, and Si atoms, respectively. (b) Ball and stick model of the propene in the cage in ITQ-12 (2 upper 4-ring oxygen atoms removed) viewed along [100], normal to the [001] diffusion pathway. Large, medium, and small balls represent O, C, and Si atoms, respectively.

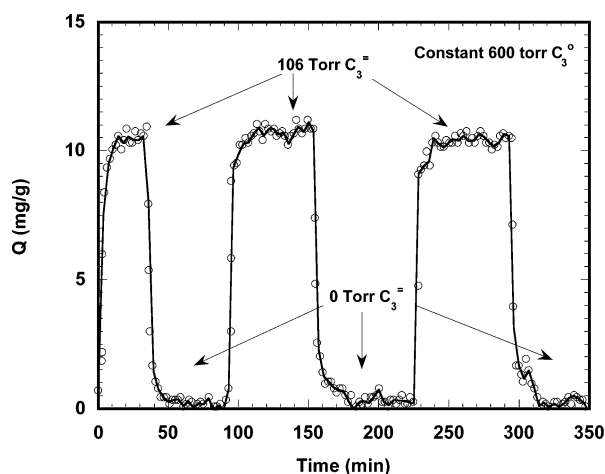


**Figure 7.** Computed effect of changes in the minimum ITQ-12 cage size on number of molecules of propene and propane sorbed, at 80 °C and  $P = 600$  Torr.

experimental observations (Figure 3), propane adsorption is one-third lower than that of propene. Propane sorption drops off sharply to near zero for a 0.3 Å decrease, whereas propene sorption decreases less dramatically with decreasing minimum cage dimension. With increasing cage size, the amount of each molecule sorbed increases to nearly the same value,  $\sim 0.85$  molecules per cage (49.6 mg propene/g). Changes in cage dimension may occur with changes in temperature and adsorption. However, to date we have been unable to document changes that conclusively support our hypothesis that the observed drop off to approximately zero propane adsorption at



**Figure 8.** Effect of preadsorbed propane on the rate of uptake of propene (at 30 °C, both gases at  $P = 600$  Torr).



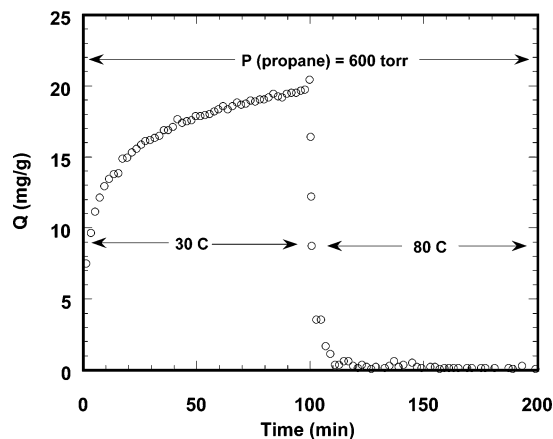
**Figure 9.** Effect at 80 °C of 600 Torr propane pressure on the rate of uptake of propene ( $P = 106$  Torr).

80 °C is due to reductions in cage size and hence thermodynamic and not kinetic factors.

**Nature of the Diffusion Process.** Diffusion in ITQ-12 is one-dimensional, with all molecules passing through the eight rings and the  $[4^5 5^4 6^4 8^4]$  ITQ-12 cages discussed above. A question of major importance is whether this one-dimensional diffusion is single file diffusion or if the  $C_3$  molecules can pass one another in the cages. Several experiments were conducted to test this.

In the first experiment, propane was adsorbed in ITQ-12 at 30 °C, 600 Torr, for 300 min, reaching a value of about 16 mg/g (Figure 8). The gas stream was then switched to 600 Torr propene, and the total sorption amount very quickly shot to ~46 mg/g at a rate indistinguishable from the rate of sorption of propene into freshly activated ITQ-12. There was no indication of any retardation of the propene adsorption rate by the preadsorption of propane.

In the second test, activated ITQ-12 was contacted at 80 °C with a flowing gas stream containing a constant 600 Torr of propane. As indicated above at this temperature propane adsorption is zero or near zero. However, if any propane is adsorbed, it would be expected to decrease the rate of sorption of propene if diffusion is single file in nature. Propene, at 106 Torr pressure, was then intermittently added to the propane gas stream. As seen in Figure 9, the propene rapidly adsorbs and desorbs indicating no retardation in the sorption rate due to propane.



**Figure 10.** Effect of temperature on propane sorption on ITQ-12 at constant propane pressure (600 Torr) with a temperature rise from 30 to 80 °C, in ~1 min, at the 100 min point.

Several similar tests were conducted but none indicated that propane produced any retardation in the rate of adsorption or desorption of propene. From this, we conclude that  $C_3$  molecules can interchange, i.e., pass, in the cages producing in effect multife diffusion. This is the only region in the structure where interchange can occur.

In a related test, propane was adsorbed at 30 °C on ITQ-12 over a 100-min period, reaching a sorption level of 16 mg/g. The sample was then quickly heated, in a ~1 min time period, to 80 °C. As seen in Figure 10 the propane very rapidly desorbs down to essentially zero. This also is consistent with the occurrence of small structural changes upon this heat up, making propane adsorption more unfavorable. This observation supports the idea that the zero propane adsorption at 80 °C is due to thermodynamic rather than kinetic factors: if it were kinetic, a slower and incomplete desorption would be expected.

**Separation Simulation.** Preliminary computer simulation of a PSA propene separation process,<sup>11</sup> based on a single adsorption chamber, has been conducted. Two feed stream compositions have been considered. The first, 80% propene/20% propane is close to the  $C_3$  hydrocarbon composition from a cracker unit. The target is 99.5% propene, i.e., polymer grade propene. The second feed, 98% propene/2% propane is assumed to be the composition of a slip-stream from the off gas of a propylene polymerization unit. Here the goal is to remove propane with minimal loss of propene and to produce 99.5% propene.

In the first simulation with the 80/20 feed, the start of cycle temperature was 80 °C, the pressure swing 4.0 atm to ~0.1 atm, and with four steps per cycle: (1) pressurization, (2) adsorption, (3) depressurization, and (4) venting to low pressure. The results show that for a 16 s pressurization plus adsorption time and a total cycle time of 50 s, 99.5% propene, amounting to 72 mol % of the propene in the feed, is produced with a productivity of ~1.6 g of propene per gram of zeolite-hour. This high purity propene meets requirements for polymerization grade propene. Also, during the adsorption step, a propane enriched stream of  $C_3$ 's amounting to 40% of the total feed stream and 97% of the propane in the feed is obtained in the output stream. Feeding this latter product to two additional beds indicates that the recovery of 99+% of the propene is possible.

In the second simulation with the 98/02 feed, the cycle design was as described above for the 80/20 feed. The results show that, during 3 s pressurization plus adsorption steps (total cycle time of 40 s), a propane enriched stream containing 73% of the propane and 4.5% of the propene in the feed is obtained. Thus, of the 100 mol of feed, 1.5 and 4.4 mol respectively of propane



and propene are removed and 94.1 mol of 99.2% purity propene rich product are recovered. The productivity is 0.7 g feed/g adsorbent-h.

**Comparisons.** Although the PSA simulation data presented above represent the early status of an assessment of how ITQ-12 would perform in a real process, the results are encouraging and a comparison with other studies is merited. We will limit our comparison to the zeolite AIPO-14 since it has been reported to sorb propene but to exclude propane.<sup>2-4</sup> AIPO-14 is a aluminophosphate zeolite having a one-dimensional channel structure defined by rings of eight tetrahedra and a propene sorption capacity reported as 1.1 mmol/g ( $\sim 46$  mg/g)<sup>2,3</sup> and 2.2 mmol/g (92 mg/g).<sup>4</sup> A temperature dependent partial irreversibility detracts from AIPO-14's attributes. As percent of adsorption capacity, this affect decreases from 72% at 30 °C to 20% at 120 °C.<sup>2,3</sup> The two reported simulations<sup>2-3,4</sup> indicate production of 99+ % propene purity and 90% and 53% recovery of propene for three-bed<sup>2,3</sup> and one-bed<sup>4</sup> processes, respectively. The authors of the latter study indicate the throughput or productivity is 0.0009 g of propene per gram of adsorbent per hour. These purities are in the range we find for ITQ-12, but our productivities are 3 orders of magnitude larger. ITQ-12 has also the potential advantages of very high thermal and hydro-thermal stability and no observed irreversible adsorption. Järvelin and Fair report that an equilibrium based, two-bed separation using zeolites 13X or 5A, and large nitrogen dilution, could achieve effective separation with a productivity of  $\sim 0.015$  g of propene/g adsorbent-hr, also far from our results.<sup>14</sup>

**Summary.** The unique light hydrocarbon adsorption properties of pure silica ITQ-12 zeolite have been studied in order to assess its potential for the separation of propene from propene/propane mixtures. The temperature dependence of the propane adsorption behavior is unique, showing an unexpectedly large decrease in the amount adsorbed as the temperature increases and leading to essentially zero propane adsorption at 80 °C. As expected, propene adsorption decreases modestly with increasing temperature; thus, the selectivity toward propene adsorption is exceedingly large at 80 °C. A decrease in the smallest dimension

of the ITQ-12 slit-shaped cage,  $\sim 3.9$  Å, as the temperature increases, is proposed to explain this behavior. The temperature-dependence of the propane adsorption is ascribed to thermodynamic rather than kinetic effects. Preadsorption of propane at 30 °C or competitive adsorption of propane/propene at 80 °C do not affect the rate of propene adsorption and the total propene adsorbed. All of these results, together with PSA simulations, confirm ITQ-12 as a very attractive adsorbent for the kinetic based separation of propene and propane to yield polymer grade propene streams.

**Acknowledgment.** We acknowledge several people who helped us with the PSA simulations using Aspen Tech Inc.'s ADSIM software: Warren Seider for the computing facilities and general support, Edward Gooding (Bryn Mawr) for initial guidance, summer student Gregory Guffanti (Brown University) for computational assistance, and Jeong-Ho Yun of Aspen Tech Inc. for several helpful suggestions.

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