We present a combined computational and experimental approach to evaluate the suitability of the ITQ-12 nanoporous material (ITW) as a propane–propylene separation device. For this, we have computed adsorption and diffusion of propane and propylene in the ITQ-12 zeolite. The propane isotherm is reproduced well, but the available propylene models in the literature are unable to describe the propylene isotherm. Newly developed force field parameters for propylene were obtained by fitting to our own experimental adsorption isotherms and validated with previous data taken from the literature. To obtain self-diffusion of propane and propylene in the zeolite, we combined the configurational-bias Monte Carlo method with rare-event molecular simulation techniques. Our results support experimental observations that point out ITQ-12 as a suitable structure for propane–propylene separation. The selectivity originates mainly from a difference in adsorption, possibly enhanced by a difference in diffusion.

**Experimental Section**

Pure silica ITQ-12 zeolite was synthesized following the reported example 2 of ref 20, consisting of hydrolyzing the appropriated amount of tetraethylorthosilicate (TEOS) in an olefin product with very good recovery.²⁻⁴,⁷,¹³⁻¹⁷,¹⁹ To our knowledge, the best propylene/propane separation performance has been obtained using ITQ-12 as a selective adsorbent. The reason could be attributed to the characteristic size and shape of the pores of this zeolite, which makes it a very good candidate to be used for this separation.¹³,¹⁸,¹⁹

ITQ-12 (ITW) is a two-dimensional small 8-membered-ring pore zeolite that was solved in the monoclinic C11m1 symmetry with unit cell parameters of \( a = 10.4364 \text{ Å}, b = 15.0183 \text{ Å}, \) and \( c = 8.8553 \text{ Å}, \alpha = 90^\circ, \beta = 105.74^\circ, \) and \( \gamma = 90^\circ, \) and cell volume \( V = 1326.76 \text{ Å}^3 \). The pore aperture of ITQ-12 along the [001] direction is \( 3.9 \times 4.2 \text{ Å} \) and \( 2.4 \times 5.4 \text{ Å} \) along the [100] direction. Then, the pore along [100] has no influence for adsorption, since its aperture is not large enough to allow the entrance of any hydrocarbon. Consequently, from the point of view of its adsorption properties, ITQ-12 can be envisaged as a one-dimensional small pore zeolite. Importantly, the 8-membered pores running along [001] give entrance to slit-shaped cages of \( 3.9 \times 9.6 \times 8.5 \text{ Å} \) dimensions.

A view of the zeolite along the three axes is shown in Figure 1.

In this work, we study the feasibility of using ITQ-12 for propane–propylene separations based on both kinetic and adsorption equilibria. The adsorption isotherms were computed using molecular simulations and compared with those obtained experimentally. The diffusion coefficients were computed using molecular simulations. In addition, the advantages and disadvantages of using available or new developed models and force fields for propane and propylene are analyzed in this work.
aqueous solution of the structure directing agent 1,3,5-trimethylimidazolium hydroxide (SDAOH). The resulting mixture was continuously stirred at ambient temperature until the ethanol produced during hydrolysis of TEOS and the required amount of water was evaporated. Then, an aqueous solution of HF was added to the above reaction gel, and the final mixture was manually homogenized. The final gel composition was 1 SiO2:0.56 SDAOH:0.56 HF:7 H2O.

The resulting gel was heated at the autogeneous pressure of the system in stainless steel autoclaves at 448 K for 14 days. The ITQ-12 zeolite was recovered by filtration and was exhaustively washed with distilled water and acetone, and finally was dried at 373 K for 12 h. The occluded 1,3,5-trimethylimidazolium organic cations were removed by calcination at 973 K, leading to a highly crystalline pure silica ITQ-12 zeolite, as was confirmed by means of the X-ray diffraction technique (Figure 1S in the Supporting Information). The adsorption capacity and pore aperture was determined by applying the Horvath–Kawazoe method to the high-resolution Ar isotherm measured at 83 K. The micropore volume was 0.154 cm³ g⁻¹, and the averaged pore aperture was 0.49 nm (Figure 2S in the Supporting Information), which is in excellent agreement with the crystallographic structure of ITQ-12, confirming that micropore volume can be accessed through the 8-membered ring of oxygen and silicon atoms. This is a very common approximation for small alkanes in all-silica zeolites. We used point charges for the silicon and the oxygen atoms of qSi = 2.05 e and qO = −1.025 e, respectively.

The adsorption isotherms were computed using configurational bias grand canonical MC simulation methods. Although our models for propane and propylene contain a maximum of four beads, the configurational bias method speeds up the equilibration and therefore it is worthwhile to use it. In order to compare with available data, most of our computed isotherms are given in excess loading versus pressure. The excess loading was obtained using the method of Duren et al. Pressures were obtained from the Peng–Robinson equation with the parameters Tc = 369.825 K, Pc = 4247660 Pa, and ω = 0.1524 and Tc = 365.57 K, Pc = 4664600 Pa, and ω = 0.1408 for propane and propylene, respectively.

One of the difficulties encountered when studying diffusion behavior in zeolites using simulation is that many processes occur outside the time scale accessible to molecular dynamics (MD), which is currently typically limited to diffusion rates in the order of 10⁻¹² m²/s. We compute zero-loading diffusion coefficients of propane and propylene in ITQ-12 by applying the dynamically corrected transition state theory method. This method has the potential to be orders of magnitude more efficient while still retaining full atomistic detail.

The propane and propylene molecules were described with united atom models, in which CH₃(sp³), CH₂(sp³), CH₂(sp²), and CH(sp²) groups are considered as single interaction centers. The beads in the chain are connected by harmonic bonding potentials. A harmonic cosine bending potential models the bond bending between three neighboring beads. The interactions between the adsorbates as well as between the adsorbates and the zeolite are described by Lennard-Jones potentials truncated at a cutoff of 12 Å and shifted so that the energy tends smoothly to zero at the cutoff. The effective Lennard-Jones interaction parameters for propane [CH₃(sp³)–CH₃(sp³)] ε/Kₐ = 56.0 K, σ = 3.96 Å; CH₃(sp³)–CH₄(sp³) ε/Kₐ = 108.0 K, σ = 3.76 Å] were taken from Dubbeldam et al. The additional parameters for propylene [CH₂(sp²)–CH₂(sp³)] ε/Kₐ = 53.0 K, σ = 3.74 Å; CH₂(sp²)–CH₂(sp³) ε/Kₐ = 93.0 K, σ = 3.685 Å] were taken from Liu et al. All these values were fitted to accurately reproduce the experimental vapor–liquid coexistence curves. Lorentz–Berthelot mixing rules were used for all mixed adsorbent–adsorbent interactions.

To keep the consistency of all interaction parameters used in this work, we used the Lennard-Jones parameters proposed by Dubbeldam et al. for describing the interactions between CH₃(sp³) and the oxygen atoms for the zeolite framework and Liu et al. for the interactions CH₂(sp²) and the oxygen atoms for the zeolite. These parameters, listed in Table 1, faithfully reproduce the experimentally determined isotherms in pure silica.
MFI-type zeolites and have been successfully extended to other types of pure silica zeolites.\textsuperscript{39,41,42} The model described by Liu et al. for propylene in zeolite is labeled in this work as (NP-Lgg-Lgz), i.e., the nonpolar model (NP) with Lennard-Jones parameters taken from Liu et al.\textsuperscript{40} for the guest–guest (propylene–propylene) denoted by Lgg and the guest–zeolite (propylene–zeolite) denoted by Lgz interaction. As we will see later on, this model fails to reproduce experimental adsorption of propylene in ITQ-12. Therefore, new developments were needed. Besides the nonpolar united atom model for propylene (NP), we described here a point charge model (PC). The guest–guest Lennard-Jones parameters for these polar models were taken from Liu et al.\textsuperscript{40} (Lgg) or developed in this work to reproduce the vapor–liquid equilibrium (VLE) curve according to our new Gutierrez-Sevillano et al. model (GSgg). The Lennard-Jones propylene–zeolite interactions for the polar model were also taken from Liu et al.\textsuperscript{40} (Lgz) or developed in this work from the fitting to experimental adsorption data (GSgz).

Changing Propylene–Zeolite Lennard-Jones Interactions (GSgz). Our first approach to reproduce experimental adsorption was to refit the CH$_2$(sp$^2$)–O\textsubscript{z} and CH(sp$^2$)–O\textsubscript{z} Lennard-Jones parameters. Following a similar strategy employed in previous works,\textsuperscript{7,38,39,43} simulations were performed first for ethene to determine the effective Lennard-Jones interaction parameters for the CH$_2$(sp$^2$) with the oxygen atoms of the zeolite framework (O\textsubscript{z}) and second for propylene to obtain the CH(sp$^2$)–O\textsubscript{z} interaction. Available experimental data for ethene\textsuperscript{18} and our own experimental isotherms for propylene in ITQ-12 were used as calibration sets (Figures 3S and 4S in the Supporting Information).

Implementing Molecular Dipoles for Propylene: Point Charge (PC) Model. As mentioned above, the available model for propylene was a nonpolar model (NP). We will show in the next section that this approximation is able to reproduce experimental adsorption in most zeolites\textsuperscript{40} but not in ITQ-12. When the zeolite–guest interactions are modified to describe the propylene in the ITQ-12 isotherm properly, we find that it fails to reproduce diffusion, providing extremely high free energy barriers. This finding forced us to develop a new model containing electrostatic interactions. A common choice is to use point charges on atoms to represent molecular electrostatics.\textsuperscript{44–46} We have implemented this model in our code, and in the next section, we analyze the way it performs when computing adsorption and diffusion properties in ITQ-12 zeolite.

The point charge model (PC) was defined using two positive charges of ($q = 0.87$ e) located in the CH$_2$(sp$^2$) and CH(sp$^2$) beads and a third negative charge of ($q = -1.74$ e) located in a dummy atom. The dummy–CH$_2$(sp$^2$) bond length (0.704 Å) was chosen in such a way that it reproduces the experimental dipole moment. We use Ewald summations\textsuperscript{47} to compute the point charge interactions. Detailed information on these models is compiled in Figure 2, and the adsorbent–adsorbate Lennard-Jones parameters used from previous available models of propane and propylene\textsuperscript{40} (Lgz) as well as those developed in this work (GSgz) are summarized in Table 1.

Results

In this section, we first analyze the obtained results using previous available models\textsuperscript{39,40} (united atom nonpolar models for propane and propylene). Second, we study the effect of variations on the Lennard-Jones parameters and the effect of adding point charges to the propylene model in order to correctly reproduce the experimental dipole. Finally, the need of a model able to accurately reproduce the VLE curve is discussed.


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<th>$\varepsilon/\kappa_B$ (K)</th>
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Figure 2. Propane and propylene models used in this work.
ITQ-12 are shown in Figure 3. At this temperature, the saturation pressure of the gases is 1.0793 MPa for propane and 1.3084 MPa for propylene. Our experimental and simulation results are compared with previous experimental data by Olson et al.\textsuperscript{18} Simulations were performed using the model and force field parameters for propane of Dubbeldam et al.,\textsuperscript{39} the (NP-Lgg-Lgz)\textsuperscript{s} model for propylene, and the anisotropic model\textsuperscript{48} for both propane and propylene. The pressure range spans from 10\textsuperscript{2} to 10\textsuperscript{5} Pa. Higher pressures involve adsorption in the liquid phase. Experimental data of the adsorption of propane in ITQ-12 zeolite were accurately reproduced using the model of Dubbeldam et al. This model is transferable to many other siliceous zeolites. Alkanes are modeled very successfully in zeolites. Therefore, any deviation between experimental and simulated isotherms would indicate a problem with the sample (pore-blocking, imperfections) or point to ITQ-12 being a "special" structure. Since this is not the case, we can focus on propylene. The newly obtained experimental isotherm for propylene is in very good agreement with the data of Olson et al.

We started with the existing models of Liu et al. and the anisotropic models\textsuperscript{48} for propane and propylene. Both models fail to reproduce the difference in adsorption between propane and propylene. The model of Liu et al. gives similar adsorption of propane and propylene, and its magnitude corresponds to the experimental isotherm of propane (it fails for propylene). The anisotropic model also is unable to signal a difference in adsorption of propane and propylene; it gives results that correspond to the experimental propylene isotherm (it fails for propane). Note that both models work in other structures, e.g., MFI, for propane\textsuperscript{49} and propylene.\textsuperscript{50}

There are two options to explain the discrepancies: (a) the experimental adsorption isotherm for propane is not equilibrated and would eventually reach the experimental propylene isotherm, (b) the experimental isotherms are correct: there is a large difference in adsorption of propane and propylene in ITQ-12. The experimental uptake curves after 700 min show a plateau for uptake of propane. If not equilibrated properly, then true equilibration is very, very slow. This is a discussion of theoretical nature, since in practice one can only use a finite amount of time. Option b implies that the Bei et al. model and the anisotropic model are unable to describe the adsorption difference of propane–propylene in ITQ-12. The simulation results for propylene are shifted 1 order of magnitude in pressure and almost overlap with the computed isotherm for propane. Similar behavior was observed at 400, 500, and 600 K (Supporting Information, Figure 5S). The similar computed adsorption obtained for propane and propylene can be attributed to the high similarity of the models used for these molecules. In both cases, we are using a nonpolar united atom model. The models used do not have charges or dipoles so propane and propylene molecules only differ in the adsorbent–adsorbate Lennard-Jones parameters. Similar adsorption using these models is an expected result because both molecules are similar in size and shape.

Next, we study one of these models, the Liu et al. model, for difference in diffusion of propane/propylene. Self-diffusion has been computed using the dynamically corrected transition state theory (dcTST). This method requires a separated study of the free energy profile on each axis of the structure. Although previous studies about ITQ-12 reveal that the channel system of the zeolite is only accessible from one of the axes,\textsuperscript{19,22,51} we study the free energy profile for the three axes. To compute dcTST diffusion, we first obtain the free energy profiles along the reaction coordinate (in this work, the cell axes are used as reaction coordinates). Second, we integrate these profiles in order to calculate the hopping rate and the TST diffusion coefficient. After that, we sample the starting configurations of the beads in the top of the barriers and using these starting configurations and a short MD simulation we calculate the transmission coefficient $\kappa$. Finally, using the $\kappa$ value obtained, we compute the dynamically corrected TST diffusion. The computed energy profiles at 303 K in the $c$ channels for propane and propylene are shown in Figure 4. Energy profiles in the $a$ and $b$ channels

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**Figure 3.** Computed adsorption of propane in ITQ-12 at 300 K using previously available models—Dubbeldam et al.\textsuperscript{39} (open down triangles), anisotropic model\textsuperscript{48} (open triangles)—and of propylene using the NP-Lgg-Lgz model\textsuperscript{s} (open circles) and anisotropic model\textsuperscript{48} (open squares). Experimental data of propylene provided by Olson et al.\textsuperscript{18} (dots) and propane (solid down triangles) and propylene (solid circles) obtained in this work are included for comparison.

**Figure 4.** Free energy profiles of (a) propane (dashed line) and propylene NP-Lgg-Lgz model (solid line) and (b) anisotropic propane (dashed line) and anisotropic propylene (solid line), computed along axis $c$ at 300 K.
were also computed and can be found in the Supporting Information (Figure 6Sa and b). The free energy profiles were obtained using the same force fields and models as Figure 3, and they show a similar qualitative behavior for propane and propylene. The barriers are extremely high along the $a$ and $b$ axes for both molecules, but they are low enough to allow diffusion along the $c$ axis. These results confirm previous works allowing the movement of both molecules along the $c$ axis but not along the $a$ and $b$ axes. The equipotential energy surfaces in ITQ-12 zeolite channels along the $x$, $y$, and $z$ directions are shown in Figure 5. According to the free energy barriers obtained, we focus the diffusion study on the $c$ axis, computing the free energy profiles for propane and propylene at different temperatures (Supporting Information, Figures 7S and 8S). Though the free energy profiles are similar from a qualitative point of view, the free energy barriers are lower for propylene than for propane at the same temperature. Since diffusion can be considered a hopping process from minima to minima, one can expect much lower diffusion for the higher barrier. Figure 4 compares the free energy profiles for propane and propylene at 300 K. A detailed analysis of these free energy profiles indicates that the propane free energy barriers are about 5$K_B T$ higher than the ones of propylene. Differences imply that propane and propylene diffusion coefficients are susceptible to be different. The obtained TST diffusion coefficient (not corrected yet) is 2 orders of magnitude higher for propylene ($1.5 \times 10^{-13} \text{ m}^2 \text{s}^{-1}$) than for propane ($1.2 \times 10^{-15} \text{ m}^2 \text{s}^{-1}$).

The transmission coefficients for both molecules were 0.15 for propylene and 0.17 for propane, leading to a final dcTST diffusion coefficient of $2.4 \times 10^{-14}$ and $2.1 \times 10^{-16} \text{ m}^2 \text{s}^{-1}$ for propylene and propane, respectively. This gives a propylene to propane diffusion ratio of 114. Differences on diffusion can be attributed to the type of channels of zeolite ITQ-12.

We can conclude that the NP-Lgg-Lgz model provides values for diffusion which are higher for propylene than for propane in ITQ-12 and it has been successfully tested for adsorption in zeolites with large and medium size channels. However, this model fails to reproduce the experimental adsorption of propylene in zeolites with narrow channels such as ITQ-12. In order to reproduce the experimental adsorption of propylene, we have followed several approaches based first on the variation of the Lennard-Jones parameters and second on the use of a polar model.

**B. Variations on the Lennard-Jones Parameters.** The adsorption isotherm of propylene computed at 300 K for the NP-Lgg-GSzg model is shown in Figure 6. The agreement between the simulation and our experimental data as well as the data of Olson et al. is now excellent. This agreement was obtained by varying the adsorbate—zeolite Lennard-Jones parameters, proving that in principle this variation is enough to reproduce experimental adsorption values. However, this model is not suitable for diffusion. Figure 7 compares the free energy profiles for propylene along the $c$ axis at 300 K using both the previous model (NP-Lgg-Lgz) and the new model (NP-Lgg-GSzg).
coefficient computed for propylene along the simulating and available experimental data. The transmission Lgg-Lgz model leads to an excellent agreement between available experimental data. As shown in the figure, the PC-obtained using this model (PC-Lgg-Lgz) and compared with molecule. Figure 8 shows the adsorption isotherm of propylene such that it reproduces the experimental dipole (0.36 D) of the atoms (0.87 e). The position of the dummy atom was chosen only involve propylene Differences between the PC-Lgg-Lgz and PC-GSgg-Lgz models for propylene (PC-GSgg-Lgz model), as shown in Figure 9. (Figure 9). Since the excess adsorption is computed in the gas phase, the PC-GSgg-Lgz model reproduces the experimental adsorption without any further refinement. To test the applicability of the model to the adsorption properties, we compare in Figure 10 the propylene adsorption isotherm obtained using the PC-GSgg-Lgz model with the one obtained using the PC-Lgg-Lgz model. These isotherms are in perfect agreement with available experimental data. At 300 K and atmospheric pressure, the computed excess adsorption is more than twice higher for propylene than for propane.

D. Polar Model for Propylene in Other Zeolites. The polar model reproduces the isotherms of propylene in ITQ-12 in contrast to the Liu et al. model. In Figure 11, we show how well the model performs for adsorption of propylene in MFI and CHA. We note the model performs just as well or perhaps even slightly better than the Liu model. It appears the ITQ-12 zeolite is more sensitive for small changes in model parameters. This is mainly due to the tight confinement of propane/propylene in ITQ-12.
The Dubbeldam model is able to accurately describe adsorption of propane in ITQ-12 (and other zeolites), and the polar model is able to describe adsorption of propylene in ITQ-12 (and other zeolites), in contrast to previous models. However, the polar model leads to high diffusivities for propane compared to propylene, while the previous models indicate a faster diffusivity of propylene compared to propane. An interesting question is whether the propane/propylene selectivity is due to adsorption or diffusion (or both). In the Supporting Information, we have shown uptake curves for propane and propylene in ITQ-12. At first sight, it appears that uptake of propylene is much faster than propane. This would be a correct conclusion if both species have similar isotherms, which they have not. Therefore, the uptake is influenced by the difference in adsorption and it remains unclear how much of this is due to difference in adsorption. Furthermore, these uptake experiments can give Fickian (transport) diffusivities, which can be orders of magnitude higher than self-diffusivities (albeit that they are equal in the limit of infinite dilution). We hope that experimental measurements using methods like NMR or QENS that can probe self-diffusivities will shed further light on this. If this new data can give Fickian (transport) diffusivities, which can be orders of magnitude higher than self-diffusivities (albeit that they are equal in the limit of infinite dilution). We hope that experimental measurements using methods like NMR or QENS that can probe self-diffusivities will shed further light on this. If this new data


Gutiérrez-Sevillano et al.