Molecular Simulation of Propane/Propylene Separation on the Metal-Organic Framework CuBTC

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Abstract

We present results of molecular simulation of pure propane and propylene, as well as their binary mixtures in the metal-organic framework CuBTC. By comparing simulated and experimental pure component isotherms we are able to describe the adsorption mechanism of these two molecules. The main difference is the existence of strong specific interactions between the open metal sites of CuBTC, freed by framework dehydration during the activation process, and the π orbitals of the propylene double bond. The net result is a moderate selectivity (up to 4) of the material for propylene adsorption. Given the current lack of experimental data for propane/propylene mixture adsorption in CuBTC, we have compared the molecular simulation results to predictions from Ideal Adsorbed Solution Theory using single-component experimental adsorption isotherms as input. Our comparison suggests that IAST is likely to adequately describe this system, and differences between the theory and simulation are probably due to shortcomings of the simplified potential model used to represent the π-metal interactions.

Keywords: Olefin/paraffin, Porous Media, MOF, Monte Carlo, Simulated Moving Bed

1. Introduction

Metal-organic frameworks (MOFs) have recently emerged as a new class of materials with enormous potential for gas storage and separation by adsorption [1-3]. Gas storage applications have been more widely studied experimentally than separations, presumably because the latter require time-consuming and expensive multi-component adsorption measurements. In this context, molecular simulation provides a useful alternative for gas separation studies. First of all, it is able to provide fundamental insight into the molecular-level mechanisms that control adsorption and selectivity of gas mixtures [4,5]. Furthermore, making use of this knowledge, molecular models of adsorption have been shown to be extremely powerful tools for achieving accurate predictions of mixture adsorption with minimal experimental input [6], even for highly non-ideal mixtures and complex adsorbents [7]. In this paper, we apply molecular simulation methods to study the separation of propylene from propane using the MOF CuBTC, also named HKUST-1 [8]. This is a separation of enormous importance for the petrochemical industry [9], but it is extremely challenging due to the physico-chemical similarities between those two molecules [10]. Adsorption processes such as pressure swing adsorption and simulated moving bed have shown promising results regarding product recovery and purity [11-13], and their optimization would strongly benefit from methods that can accurately predict multi-component adsorption of propane/propylene mixtures.

CuBTC is one of the few MOF materials that are already commercially available, under the trademark Basolite ® C300, which makes it a well-placed material for application in industrial adsorptive separations. It is composed of copper dimers coordinated to the oxygen atoms of benzene-1,3,5-tricarboxylate (BTC) linkers, forming a regular porous network with a high specific pore volume [8]. After synthesis, the remaining coordination sites (one per Cu atom) are occupied by water molecules, which can be removed by activation under vacuum, leaving a framework with unsaturated metal sites. It is interesting to note that a recent trend in MOF research has focused on materials with open metal sites, since these often show increased selectivity for certain components,

and open the possibility of fine-tuning the adsorbent-adsorbate affinity [14-16]. Here we explore these properties in the context of propane/propylene separations.

To our knowledge, the first molecular simulation study in CuBTC was carried out for argon adsorption by Vishnyakov et al. [17]. Since then, the majority of simulation studies have focused on small gases, including H_2, Ar, N_2, O_2, CO_2, CH_4 and H_2O (see review by Keskin et al. [18] and references therein). A few of these studies reported adsorption predictions for binary mixtures of some of these gases on CuBTC [19-24]. Since experimental binary data are not yet available for these systems, the simulation predictions were compared to the results of Ideal Adsorbed Solution Theory (IAST) [25]. In most cases, good agreement was obtained [19,20], while in a few cases, the two sets of predictions differed widely [19], but the reasons for the discrepancies were not fully explored.

We are aware of only three previous simulation studies dealing with adsorption of larger molecules in CuBTC. Chmelik et al. [26] simulated the adsorption of alkanes of different length, but focused mainly on diffusion mechanisms inside the MOF framework. García-Perez et al. [27] compared simulated and experimental propane adsorption, with simulation significantly overestimating adsorption, particularly at high temperatures. Recently, we have reported a combined experimental and simulation study of propane, propylene and isobutane adsorption on CuBTC, highlighting the different adsorption mechanisms for each adsorbate and demonstrating the potential of this MOF for use in adsorptive separations [28]. In this paper, we extend these studies to report predictions of binary propane/propylene adsorption on CuBTC from molecular simulation. The results are compared to IAST predictions using single-component experimental adsorption isotherms as input, and the differences between the two methods are discussed. Details of the simulation methods and molecular models employed are given in section 2. In section 3, we first present and discuss the comparison between simulated and experimental pure-component adsorption isotherms, and then move on to discuss the predictions for binary propane/propylene mixtures. Finally, section 4 presents our main conclusions.

2. Simulation Details

In this work, the CuBTC structure was modeled by a rigid all-atom representation of a single unit cell based on the crystal structure of Chui et al. [8], which is depicted in Figure 1a. The pore structure consists of two types of cages: i) large main cavities (8 per unit cell), connected to each other by nearly square windows of ca. 9 Å edge, and ii) small octahedral-shaped pockets (8 per unit cell), accessible from the main cavities through small triangular windows whose inscribed circle is approximately 4.6 Å in diameter (without taking the Van der Waals diameters of the framework atoms into account). The key structural characteristic is a copper dimer with a Cu-Cu distance of 2.63 Å. These dimers are coordinated to the oxygen atoms of the BTC linkers in a paddlewheel arrangement (Figure 1b). The remaining coordination sites (one per Cu atom) are occupied by water molecules, bonded axially to the copper. Prior to experimental measurements of adsorption [28], these water molecules are removed by an activation procedure. Thus, the corresponding oxygen atoms present in the original crystal structure were also removed in our simulations, so as to represent a dehydrated CuBTC sample. This dehydration leaves unsaturated Cu sites available for adsorption, which, as we will see later, have a significant impact on the adsorption selectivity of CuBTC. Although it has been reported [29] that the CuBTC structure changes upon dehydration, these changes are slight (a small reduction of the Cu-Cu distance and a 1.33% shrinkage of the unit cell volume). For this reason, and because the dehydrated crystal structure has not yet been reported, we have used the original coordinates of Chui et al. [8].

Figure 1

Propane and propylene molecules were modeled using a united-atom description, i.e. considering each CH_x group as a single interaction center with effective potential parameters. Using this approach, propane is composed of two $CH_3(sp^3)$ and one $CH_2(sp^3)$ centers, while propylene contains one $CH_3(sp^3)$, one $CH(sp^2)$ and one $CH_2(sp^2)$ center. Each site is electronically neutral and interacts by a Lennard-Jones 12-6 potential with other adsorbate and framework sites. Parameters

for alkane sites were taken from the work of Dubbeldam et al. [30], while those for alkenes were taken from Jakobtorweihen et al. [31]. These parameters result from a reparameterization of the standard TraPPE-UA force field [32,33] for use in adsorption studies, and provide very good agreement with experimental adsorption data of propane and propylene in zeolites [30,31,34,35]. All bond lengths were considered to be rigid, while bond angles were allowed to bend according to a harmonic angle potential, with parameters taken from the TraPPE-UA force field [32,33].

Lennard-Jones potential parameters for CuBTC were taken from the DREIDING force field [36], except those for the Cu atom, which were not available in DREIDING and were thus taken from the UFF force field [37]. These parameters were shown to accurately describe hydrocarbon adsorption in IRMOF-1 and IRMOF-6 [38], which are built from the same type of organic ligand as CuBTC. However, in a previous paper, we have observed the existence of strong specific interactions between the unsaturated Cu sites and the carbon-carbon double bond of propylene, which are not adequately captured by standard force fields (see full discussion of this effect in section 3.1). In order to account for this effect in a simplified way, we have modified the Lennard-Jones well depth for the interaction between Cu and the sp^2 sites of propylene. Interactions between different sites were computed from the standard Lorentz-Berthelot combining rules, and all interactions were cut off at a distance of 1.3 nm. Table 1 provides the full list of Lennard-Jones parameters used in this work.

Table 1

All simulations presented here were performed using the latest available version of the open-source MUSIC simulation software [39]. Equilibrium adsorption isotherms were calculated by grand canonical Monte Carlo (GCMC), in which the temperature (T), volume (V) and chemical potential (μ) of the system are kept fixed, while the total number of molecules (N) fluctuates. Apart from the standard translation and rotation trials, we have used energy-biased and cavity-biased insertion and deletion trials, which significantly improve the efficiency of molecule exchange and are essential to obtain accurate results at high coverage. Energy bias [40] works by preferentially

inserting molecules in the energetically more favorable regions of the solid, while cavity bias [41] probes regions where the sorbate molecules leave large enough cavities to accommodate a new molecule. For each isotherm point, the system was equilibrated during 5000000 steps, followed by 5000000 sampling steps for data collection. The chemical potential was converted to pressure (P) by applying the Peng-Robinson equation of state. In order to compare the simulated isotherms to experimental data, the former must be converted from absolute to excess adsorbed amount. We follow the approach of Myers and Monson [42], and calculate the difference between absolute and excess adsorption from the second virial coefficient for Helium adsorption.

3. Results and Discussion

3.1 Pure component adsorption

In Figure 2, we compare simulated and experimental adsorption isotherms of propane on CuBTC at several temperatures. The experimental data were taken from our previous work [28]. The simulated isotherms have the same shape as the experimental isotherms, but there appears to be a systematic overestimation of the amount adsorbed, particularly at high pressures. We have considered the possibility of this being due to an inability of propane molecules to access the small octahedral pockets from the large cages via the narrow triangular windows (see section 2). This type of bottleneck is not accounted for in standard GCMC simulations, since molecule insertions are attempted in the whole volume with equal probability. Thus, if a molecule is small enough to fit in the pockets, but too large to diffuse through the windows, the result would be an overestimation of the amount adsorbed in the simulations relative to the experiments. Using this reasoning, we were able to explain the mechanism of adsorption of isobutane in CuBTC [28]. However, this is not the case with propane – simulations performed in a CuBTC structure with blocked pockets resulted in a significant underestimation of the adsorption at low pressures [28]. Furthermore, contrarily to isobutane, which is a branched hydrocarbon, propane is linear and its radial cross-section is small enough to squeeze through the triangular windows. Snapshots obtained during the pure propane

adsorption simulations are shown in Figure 3. We can see that propane adsorption occurs preferentially in the octahedral pockets at low pressure (Figure 3a) and in both types of pore at high pressure (Figure 3b). Thus, a more likely explanation is that the simulations overestimate adsorption because they are performed on a pure infinite CuBTC crystal structure, while the actual material used in the experiments may contain impurities. Another possibility is the difficulty in reaching equilibrium in the propane adsorption experiments at high coverage, which is a well documented phenomenon in zeolites composed of both small and large cages connected by small windows [43].

Figure 2

Figure 3

Simulated and experimental adsorption isotherms for propylene on CuBTC are shown in Figure 4. Comparing the experimental isotherms with those for propane (Figure 2), it is clear that propylene is the most adsorbed gas in the entire range of temperatures and pressures. Furthermore, we have reported that the isosteric heat of adsorption for propylene is higher than that for propane and decreases with coverage, while the Henry's constant of adsorption is also much higher for propylene [28]. These facts point to the existence of a strong specific interaction of this adsorbate with the CuBTC framework. Indeed, it is well known that π-complexation bonds are formed between transition metals of the main group (which includes Cu) and unsaturated hydrocarbons [44]. These bonds result from σ-donation of electrons from the bonding π-orbital of the olefin to the vacant *s*-orbital of the metal, together with back-donation from *d*-orbitals of the metal to the antibonding π^*-orbital of the olefin. Interactions of this type have been reported in recent IR spectroscopic studies of adsorbed gases with unsaturated bonds (CO, CO_2 and NO) in dehydrated CuBTC frameworks [45]. They were also invoked to justify the preferential adsorption of isobutene over isobutane in this material [46].

Figure 4

Simulations of pure propylene adsorption performed previously using the normal interaction parameters for the CuBTC framework resulted in a very significant underestimation of the amount

adsorbed (up to 70%) [28]. This is because standard force fields are unable to account for the specific interaction between the π-orbitals of the sp^2 sites of propylene and the unsaturated metal sites. Indeed, the DREIDING and UFF force fields describe only van der Waals interactions between the adsorbate and adsorbent sites, which are particularly weak when they involve copper atoms (see low value of ε for this atom in **Table 1**). As a simplified approach for describing these specific interactions, we have manually adjusted the value of ε for Cu interacting with the sp^2 sites of propylene, maintaining the standard combination rules, so that the simulations matched the experimental value for adsorption of pure propylene at 323 K and 10 kPa. The resulting value of ε/k_B was 875 K (see Table 1), which results in a total interaction energy between Cu and the two sp^2 sites of the order of 16 kJ/mol, well within the expected range for π-metal interactions [47]. Using this modified interaction potential, we were able to obtain reasonable agreement between simulation and experiment at all temperatures (Figure 4), strongly suggesting that the high uptake of propylene is indeed due to strong specific π-Cu bonds.

Figure 5

Our hypothesis is supported by the experimental adsorption data, as mentioned above, and by visual inspection of the powder samples after adsorption of the different hydrocarbons – when loaded with propane the powder showed a deep blue color, while samples loaded with propylene showed a distinctive turquoise color, similar to that of the hydrated sample. It is well known that copper complexes change color according to the degree of metal coordination [48], and thus these observations also suggest that propylene occupies the coordination sites left vacant after the removal of water molecules. Snapshots of pure propylene adsorption, obtained from the simulations, are shown in Figure 5. Like propane, propylene adsorbs in the octahedral pockets at low pressure, but there is now an additional preferred site, directly adjacent to the unsaturated Cu atoms (see Figure 5a). The presence of this additional strong adsorption site causes a significant enhancement of adsorption at intermediate and high pressures (Figure 5b), compared to propane (Figure 3b).

3.2 Binary adsorption equilibrium

As we have seen in the previous section, molecular simulation using rather simple models is able to describe adsorption of pure propane and propylene on CuBTC, although agreement is not perfect. It would be extremely interesting to find out how the simulations would perform in the prediction of multi-component adsorption. For that purpose, we have carried out molecular simulations of adsorption isotherms of an equimolar propane/propylene mixture in CuBTC at 373 K, and the results are shown in Figure 6. As would be expected from the pure-component isotherms, propylene is more strongly adsorbed than propane throughout the entire pressure range.

Figure 6

The adsorbed amount of each species from a binary mixture can be contrasted against the amount adsorbed of the pure component at the same partial pressure as in the mixture. The latter is easily obtained from the simulated pure component isotherms of each species, multiplying the pressure by the bulk mole fraction of the respective components in the mixture. These "equivalent pure-component" isotherms are shown in Figure 6 as open symbols for the equimolar mixture at 373 K. At low pressure they are practically indistinguishable from the simulated binary isotherms, which suggests that both species are adsorbing independently of each other under these conditions. In other words, the affinity of CuBTC for a given component is not significantly affected by the presence of the other component. This is a reasonable expectation, since low-pressure adsorption is mainly controlled by adsorbent-adsorbate interactions, while adsorbate-adsorbate interactions are relatively unimportant. Simulation snapshots for the binary mixture at low pressure (Figure 7a) show that the octahedral pockets are occupied by both propane and propylene molecules, while propylene also adsorbs onto the unsaturated metal sites. Thus, the adsorption mechanism at low pressures is the same as observed in the pure component simulations. As the pressure increases, however, the available space inside the pore network becomes scarce, and packing effects, as well

as adsorbate-adsorbate interactions, become relevant (Figure 7b). At these conditions, the simulated binary isotherms deviate downward from the equivalent pure-component estimates (Figure 6).

Figure 7

Unfortunately, there are no available experimental data for binary propane/propylene mixtures on CuBTC against which our simulations can be compared. We have thus decided to compare our simulations against predictions obtained by applying IAST to the experimental pure component isotherms. This theory assumes that the spreading pressures calculated from the Gibbs adsorption isotherms are equal for the two components at equilibrium [25]. Further assuming unity activity coefficients for all components of the mixture yields the following equality for a binary system:

$$\int_0^{P_1^0} \frac{q_1}{P} \mathrm{d}P = \int_0^{P_2^0} \frac{q_2}{P} \mathrm{d}P \tag{1}$$

where q_i is the amount adsorbed of species i, and P_i^0 is the equilibrium "vapor pressure" for adsorption of pure i at the same spreading pressure and temperature as the mixture. This equation is solved together with Raoult's law for both components:

$$Py_i = P_i^0 x_i \tag{2}$$

where x_i is the mole fraction of component i in the adsorbed phase, and y_i is the corresponding mole fraction in the bulk phase. To perform the integrations in equation (1), we have fitted the pure component adsorption isotherms to the Dual Site Sips (DSS) model, which has the form:

$$q_i = q_{m,i,A} \frac{\left(b_{i,A}P\right)^{1/\eta_{i,A}}}{1+\left(b_{i,A}P\right)^{1/\eta_{i,A}}} + q_{m,i,B} \frac{\left(b_{i,B}P\right)^{1/\eta_{i,B}}}{1+\left(b_{i,B}P\right)^{1/\eta_{i,B}}} \tag{3}$$

In this model, q_m is the maximum loading capacity of the sorbent, b is the affinity parameter and η is the solid heterogeneity parameter; subscripts A and B refer to two distinct adsorption sites. The optimal fitting parameters were obtained by minimizing the sum square of residuals between the experimental data and the DSS equation through an optimization routine in the MATLAB software

(7.3). The reader is referred to our previous paper [28] for further details regarding these fits, including values of the fitting parameters.

In Figure 8, we show simulated adsorption isotherms for propane/propylene mixtures with variable composition at two fixed pressures, together with the corresponding binary IAST predictions using single-component experimental isotherms as input. At a pressure of 100 kPa (Figure 8a), the total amount adsorbed lies well above the IAST results in the entire composition range. This reflects the overestimation of the pure component isotherms observed at high pressure (see Figures 2 and 4). Thus, a more useful comparison is obtained at 50 kPa (Figure 8b), where the pure component simulations are much closer to the experimental values. In this case, the total adsorbed amount in the mixture is quite close to the IAST predictions. Nevertheless, the isotherms for the individual components do not show very good agreement – propane adsorption is overestimated by the simulations, while propylene adsorption is underestimated.

Figure 8

One can also calculate adsorption selectivities from the predicted binary adsorption isotherms. The selectivity (S) for component 1 relative to component 2 is defined as:

$$S_1 = \frac{x_1 y_2}{x_2 y_1} \tag{4}$$

Propylene selectivities obtained from simulations and IAST are shown in Figure 9a for fixed composition and variable pressure, and in Figure 9b for fixed pressure and variable composition. The selectivity is extremely sensitive to small variations in the amounts adsorbed, and thus the disagreement between both prediction methods becomes even more evident, with IAST predicting a much higher selectivity of CuBTC for propylene adsorption.

Figure 9

Given the absence of experimental data, it is hard to tell whether the discrepancy between predictions from molecular simulation and IAST is due to an inability of IAST to accurately describe this system or to inadequacies in the molecular model. Nevertheless, a strong clue can be

gleaned by comparing both curves to predictions of binary adsorption obtained by applying IAST to the simulated pure-component isotherms, rather than to the experimental data. Such predictions are shown as dashed lines in Figure 9. Apart from the region at very low pressure, these "simulation" IAST predictions closely agree with the results obtained by directly simulating binary equilibrium (full circles in Figure 9), which suggests that IAST may provide an accurate description of binary propane/propylene adsorption equilibrium in CuBTC. If this is indeed the case, then IAST predictions based on the experimental pure component isotherms (open triangles in Figure 9) are likely to be close to the actual experimental binary values, and the differences observed between simulation and IAST are probably due to shortcomings of the molecular models used.

We see two possible reasons for the failure of the simulations to match the IAST predictions based on experimental pure-component data. One, already discussed, is related to possible differences between the "virtual" material, a perfect CuBTC crystal, and the actual adsorbent, which probably contains a certain degree of impurities, residual solvent molecules and/or inaccessible portions of the pore volume. This effect is a strong candidate to explain the overestimation of pure propane adsorption by molecular simulation (Figure 2). Assuming that a certain portion of the material is either inert or inaccessible to hydrocarbon adsorption, this effect could be corrected by simply multiplying the adsorbed amount of each species by a constant scaling factor. However, it is clear from Figure 8 that, although this would markedly improve the simulation predictions of the total amount adsorbed, the isotherms for the individual components would still significantly disagree with IAST.

Another possibility is an inadequate description of the specific π-Cu interactions by our simplified potential model. In fact, it is unlikely that such an interaction can be fundamentally described by a simple Lennard-Jones 12-6 functional form. Instead, the potential function probably contains two partially overlapping wells, one due to dispersive forces and another one (much deeper and at a closer distance) due to the π-Cu attraction. Furthermore, the range of this specific attraction is likely to be significantly shorter than that of Van der Waals interactions. Our modified Lennard-

Jones well depth is accounting for all these factors in an effective way. Although it does a good job at modeling pure propylene adsorption at several temperatures, it clearly lacks physical realism, and this may be hindering its performance in multi-component adsorption prediction. In summary, the observed differences between simulation and IAST are probably due to a combination of both effects discussed here. It is thus essential that a more chemically consistent approach for describing adsorption in MOFs with open metal sites be developed. It is possible that this could be achieved by including partial charges in the framework and adsorbates [22] or by adding a specific potential term for π-metal bonds [49].

4. Conclusions

In this paper, we present a systematic molecular simulation study of the adsorption of propane, propylene and their binary mixtures in the metal-organic framework CuBTC. Comparison of simulated and experimental pure component isotherms showed that at low pressure both molecules adsorb preferentially in the small octahedral pockets of the framework, and begin to occupy the large cages as the pressure increases. Furthermore, strong specific interactions between the π orbitals of propylene and unsaturated metal sites, left vacant after the removal of weakly-coordinated water molecules in the activation process, were clearly identified. These specific interactions are the primary cause of the enhanced affinity of CuBTC for propylene, leading to moderate selectivities toward this adsorbate. These interactions were modeled in an approximate way by use of a modified Lennard-Jones well depth between Cu atoms and hydrocarbon sp^2 sites, and this model showed good agreement for pure propylene adsorption at several temperatures. Overestimation of propane and propylene adsorption at high pressures in the simulations could be due to the existence of impurities or inaccessible volume in the real material.

We have also reported predictions of binary adsorption of propane/propylene mixtures, using both molecular simulation and Ideal Adsorbed Solution Theory with single-component experimental isotherms as input. The two sets of predictions disagree significantly, particularly

when selectivities are concerned. One possible reason is related to the differences between the virtual and the real material, as discussed above. Another reason is due to shortcomings of the simplified molecular model used to describe the π-metal interactions between Cu and propylene. Given the importance of unsaturated metal sites in enhancing the selectivity of MOF materials, demonstrated in this work and in previous studies [14-16,28], a more chemically reasonable description of the specific interactions between these sites and adsorbate molecules is essential. Our comparative analysis suggests that IAST is likely to provide a reasonable description of adsorption of propane/propylene mixtures in CuBTC. If this is the case, selectivities for propylene of about 4 may be attained experimentally. It would be highly desirable that experimental measurements of multi-component adsorption in CuBTC be performed to test the validity of these predictions.

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Table 1. Lennard-Jones potential parameters for hydrocarbons and CuBTC atoms

Site	σ (nm)	ε/k_B (K)
CH_3 (sp^3)	0.3760	108.00
CH_2 (sp^3)	0.3960	56.00
CH_2 (sp^2)	0.3675	85.00
CH (sp^2)	0.3730	47.00
Cu	0.3114	2.514 (875[a])
O	0.3033	48.16
C	0.3476	47.86
H	0.2846	7.650

[a] Modified value for interaction with sp^2 sites.

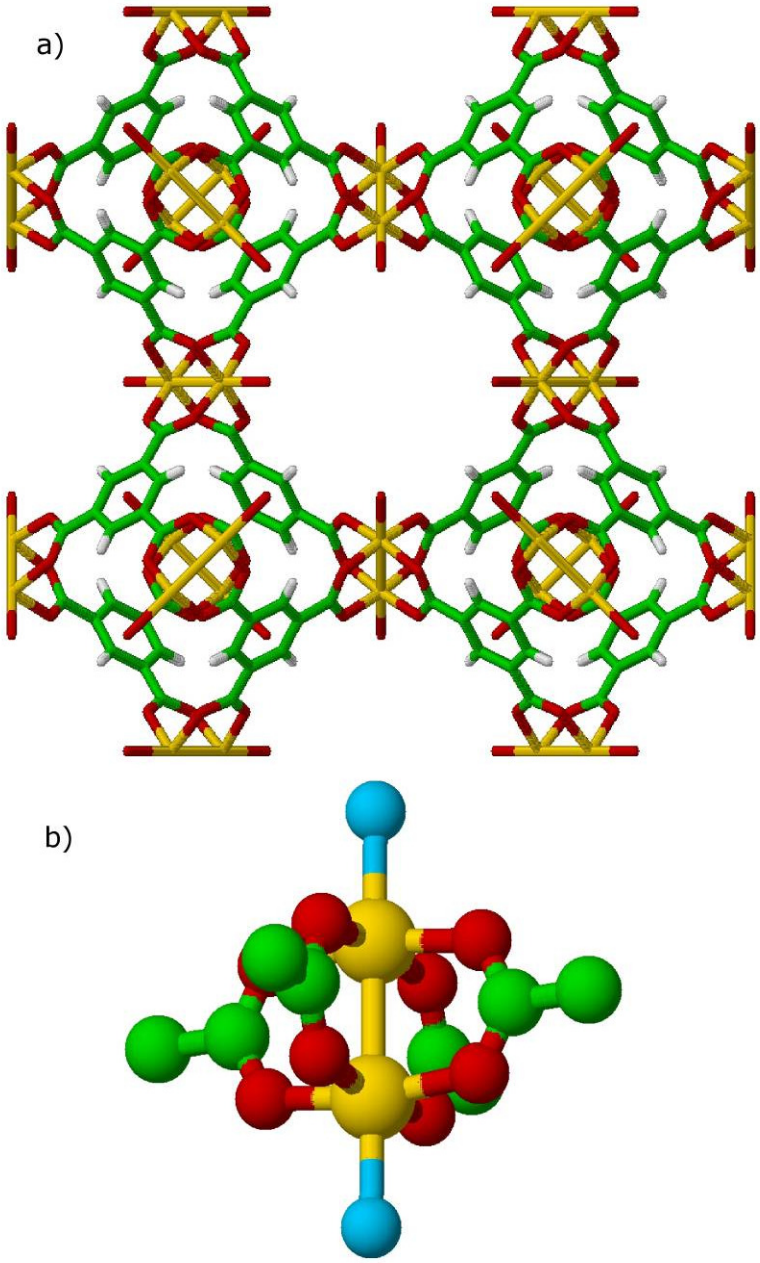

Figure 1. a) Framework structure of CuBTC viewed along the [100] direction (Color code: yellow = copper, red = oxygen, green = carbon, white = hydrogen); b) Detailed structure of the Cu paddlewheel unit, where axially-bonded water oxygen atoms are represented in light blue.

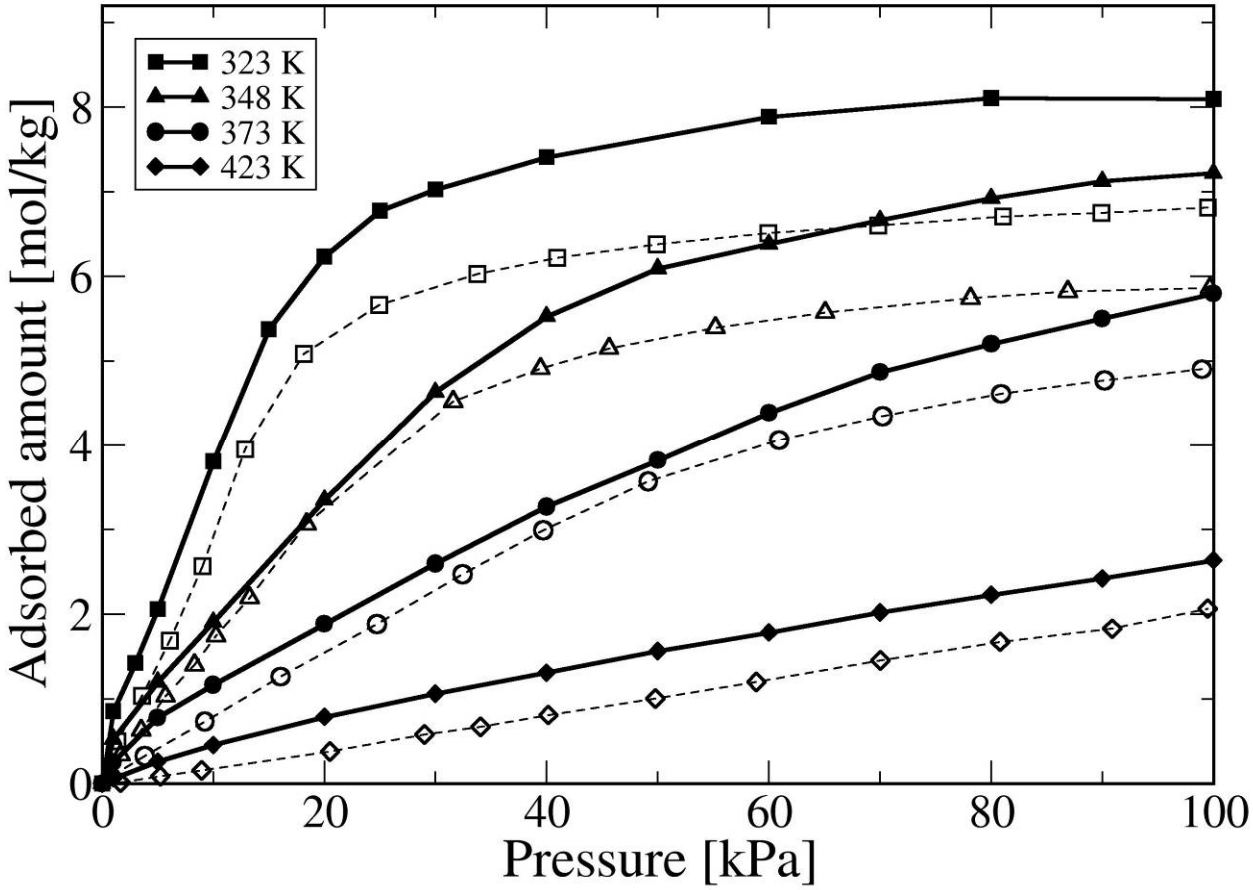

Figure 2. Comparison between experimental (open symbols and dashed lines) and simulated (full symbols and solid lines) propane adsorption at different temperatures.

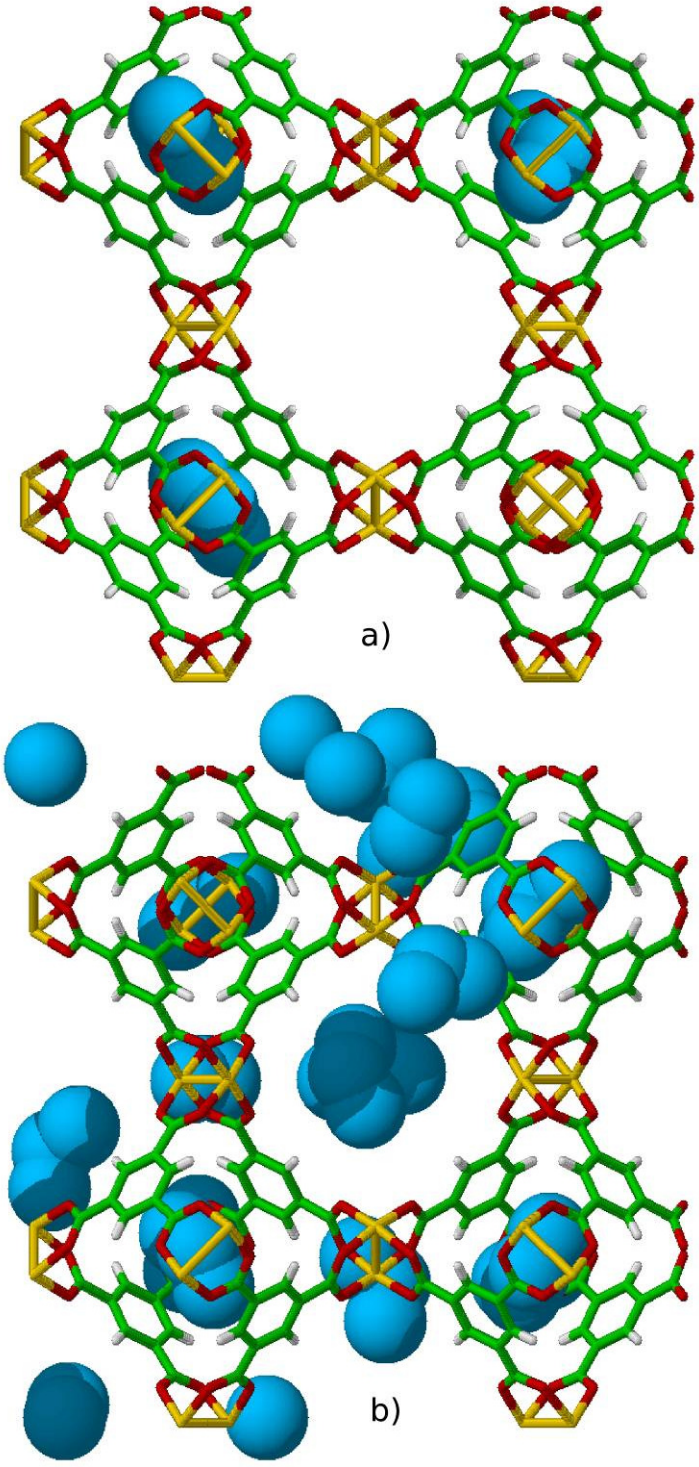

Figure 3. Snapshots obtained during adsorption simulations of propane in CuBTC at 373 K and: a) 5 kPa; b) 30 kPa. Color coding for the framework atoms is the same as in Figure 1a, and propane sites are shown as light blue spheres.

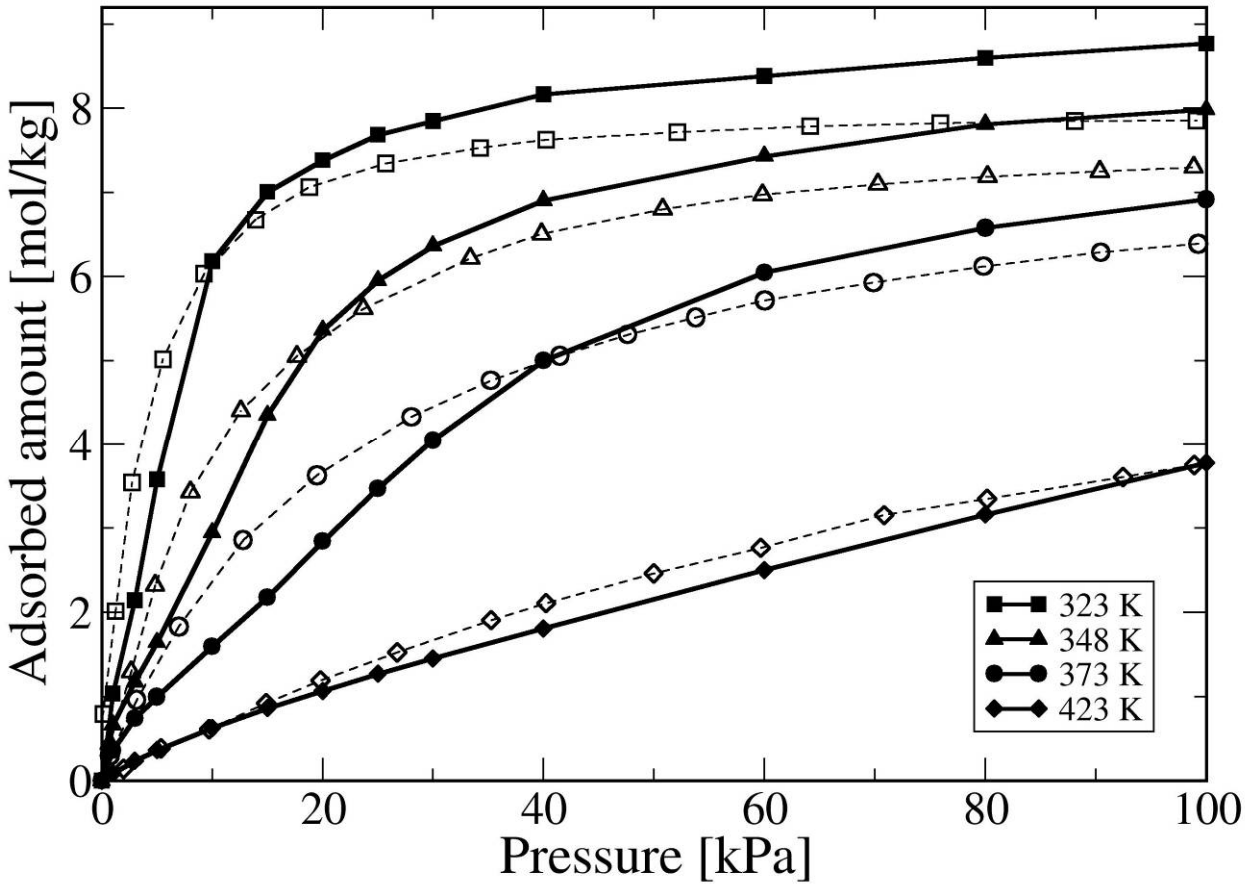

Figure 4. Comparison between experimental (open symbols and dashed lines) and simulated (full symbols and solid lines) propylene adsorption at different temperatures.

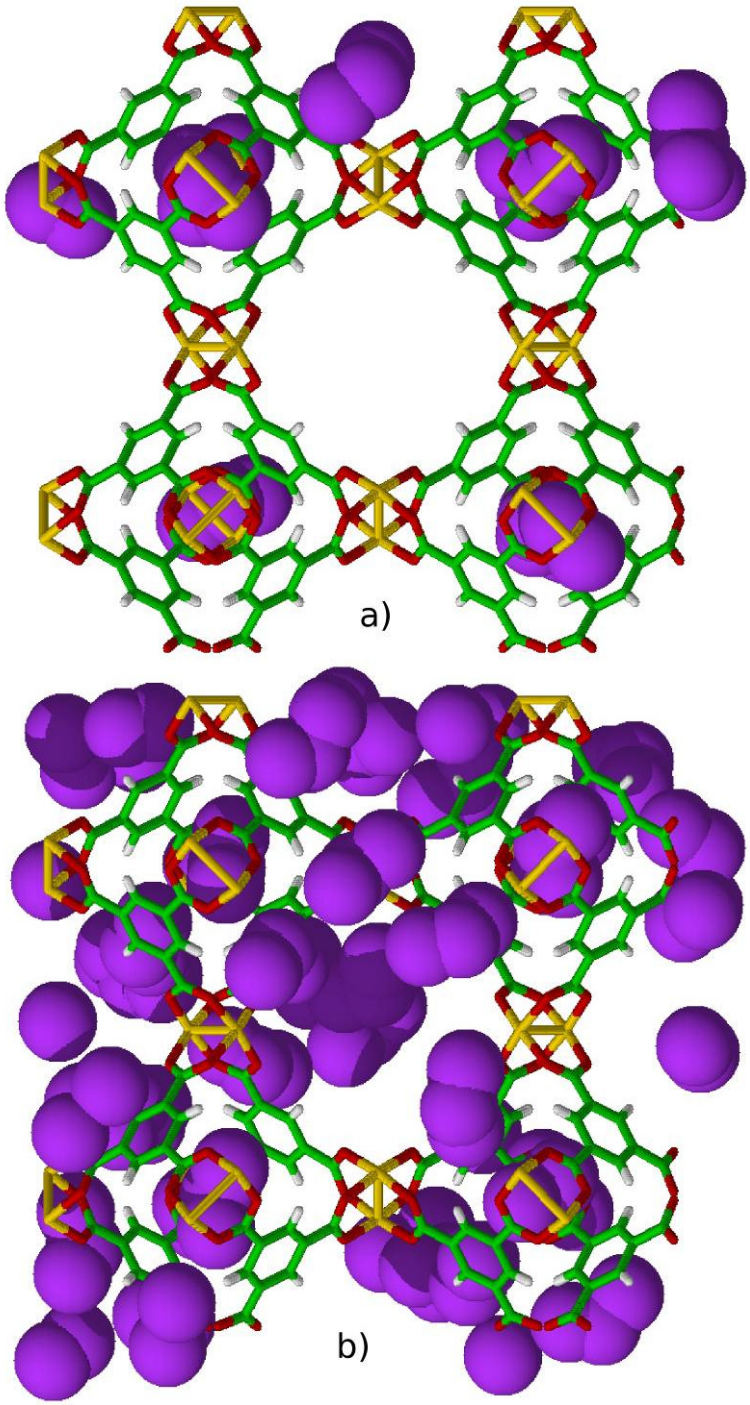

Figure 5. Snapshots obtained during adsorption simulations of propylene in CuBTC at 373 K and: a) 5 kPa; b) 30 kPa. Color coding for the framework atoms is the same as in Figure 1a, and propylene sites are shown as purple spheres.

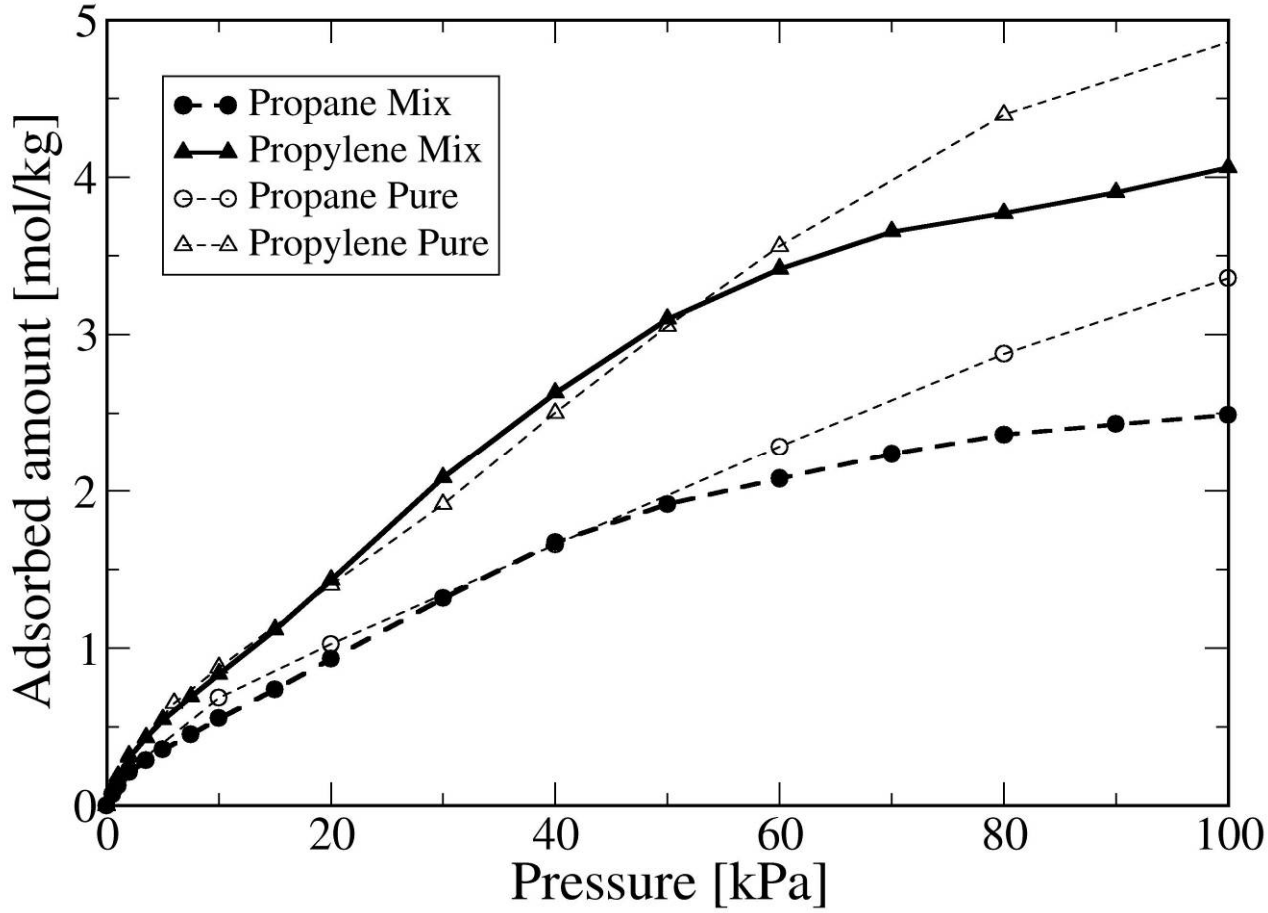

Figure 6. Simulated adsorption isotherms for an equimolar mixture of propane (full circles and solid lines) and propylene (full triangles and dashed lines) in CuBTC at 373 K. Also shown, as open symbols, are the corresponding pure-component isotherms at a partial pressure equivalent to the binary mixture (see text for details).

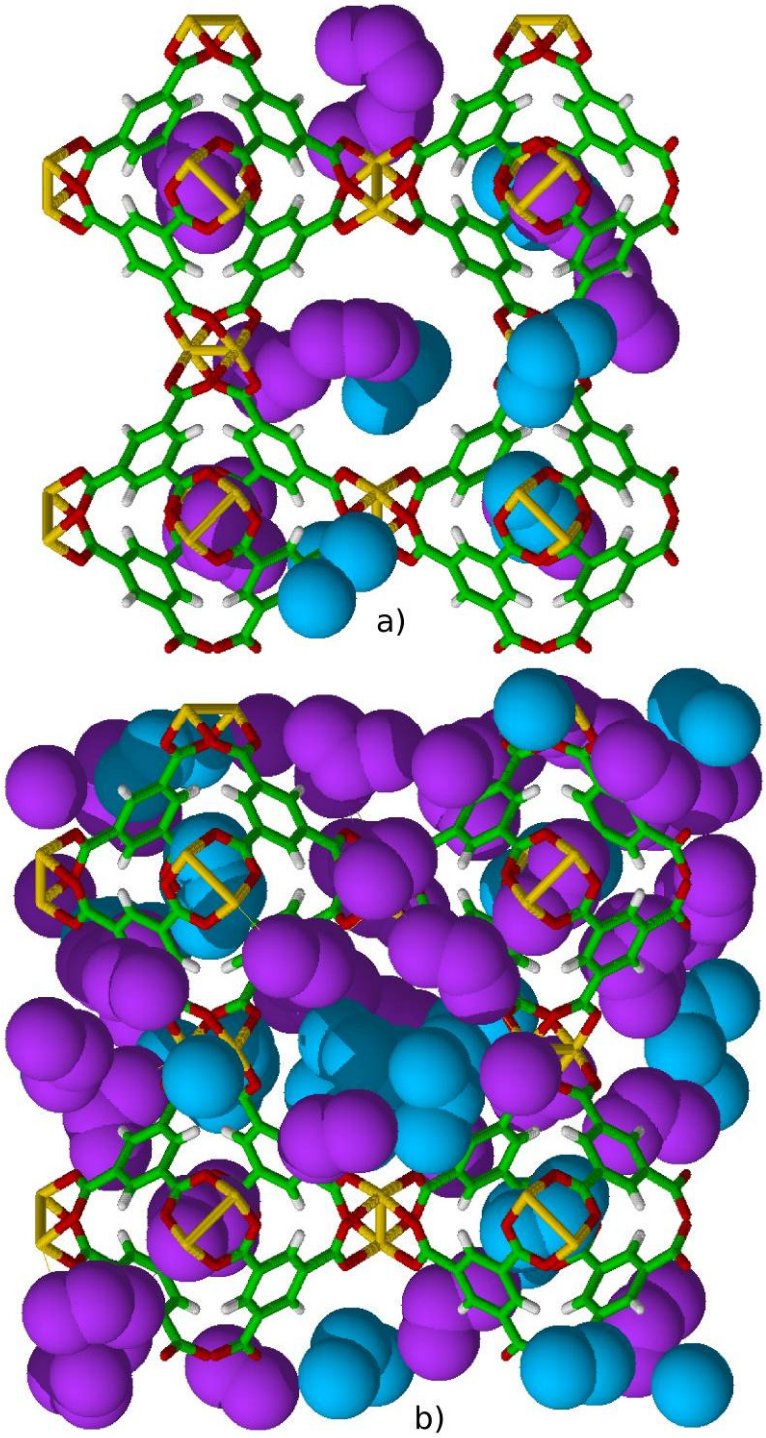

Figure 7. Snapshots obtained during adsorption simulations of an equimolar mixture of propane and propylene in CuBTC at 373 K and: a) 10 kPa; b) 60 kPa. Color coding is the same as in Figures 3 and 5.

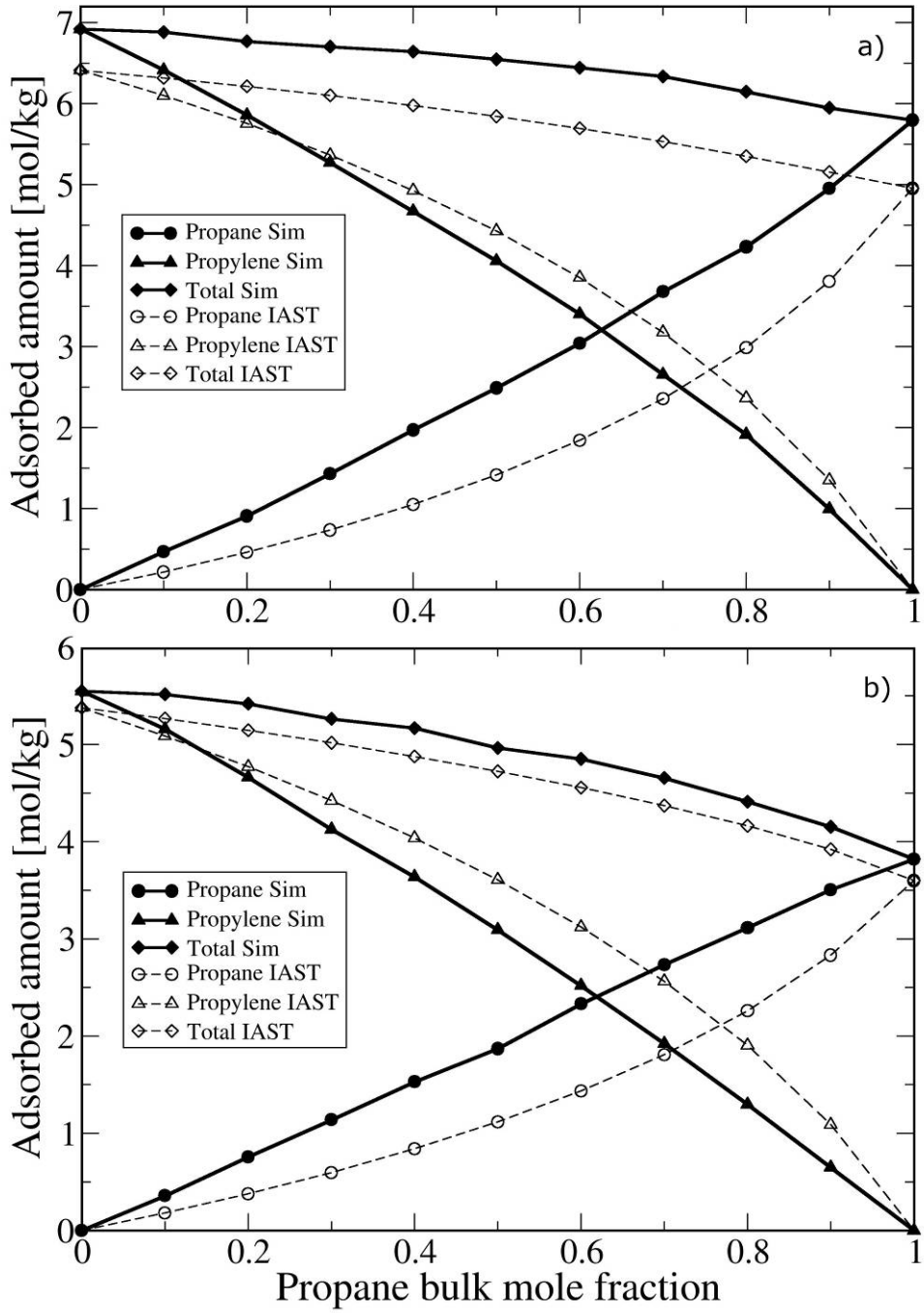

Figure 8. Comparison between molecular simulation (full symbols and solid lines) and IAST (open symbols and dashed lines) predictions for adsorption of binary propane/propylene mixtures of variable composition in CuBTC at 373 K and a pressure of: a) 100 kPa; b) 50 kPa.

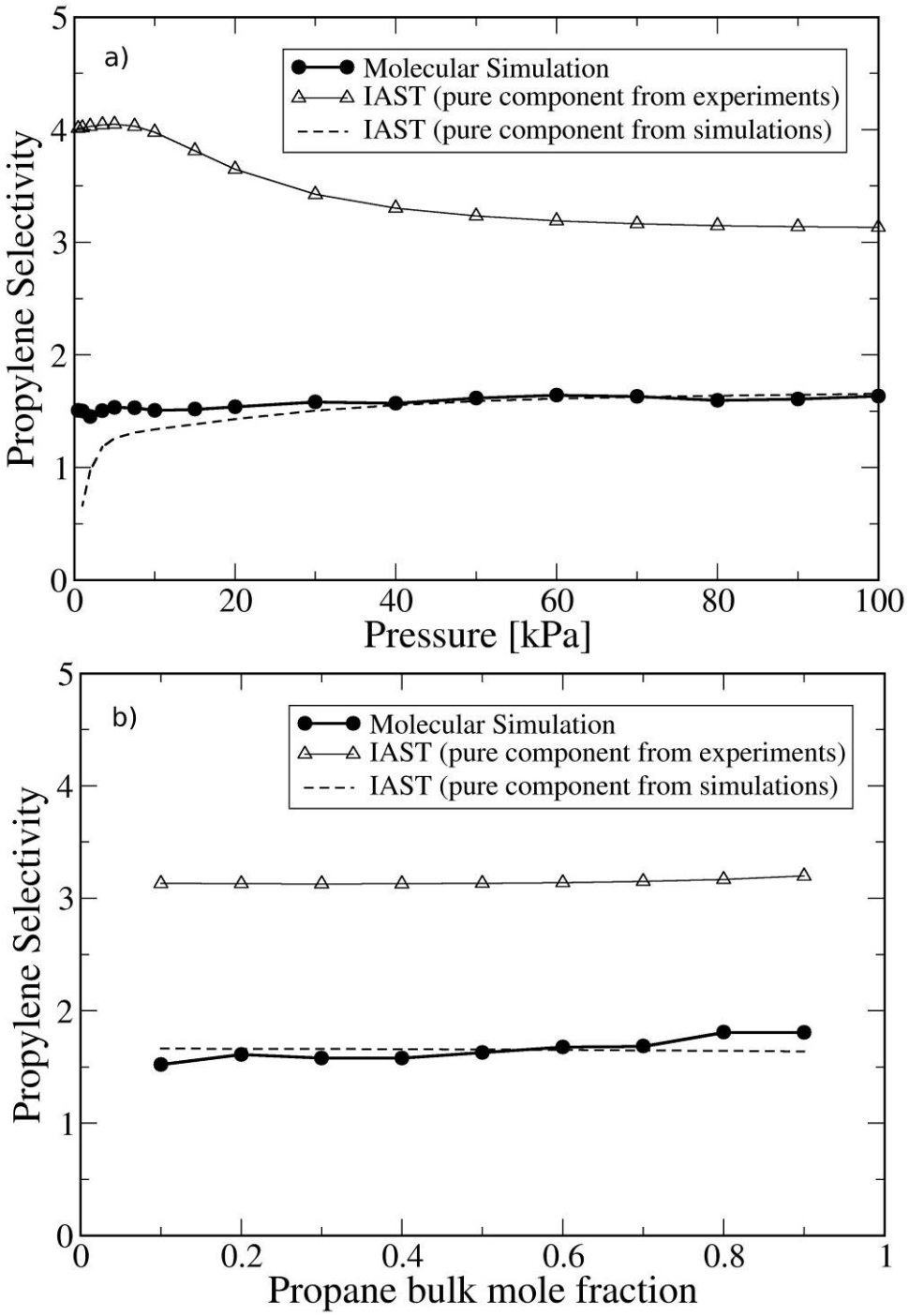

Figure 9. Comparison between molecular simulation (full symbols and thick lines) and IAST (open symbols and thin lines) predictions for the selectivity of binary propane/propylene mixtures in CuBTC at 373 K and: a) fixed composition at 0.5 bulk propane mole fraction and variable pressure; b) fixed pressure at 100 kPa and variable composition. Also shown, as dashed lines, are predictions using IAST but based on the simulated pure-component isotherms rather than on the experimental isotherms.