Comment on "Modeling Adsorption and Self-Diffusion of Methane in LTA Zeolites: The Influence of Framework Flexibility"

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Received: August 22, 2010

In a recent paper by García-Sánchez et al.,[1] the influence of framework flexibility on the self-diffusivity, $D_{i,self}$, of CH_4 has been investigated in three different zeolites with the LTA topology, LTA-Si (all-silica), ITQ-29 (all-silica), and LTA-5A (96 Si, 96 Al, 32 Na^+, 32 Ca^{2+}, Si/Al = 1). Two different force fields, due to Hill and Sauer[2] and Nicholas et al.,[3] were used to describe the framework flexibility. For a range of CH_4 loadings, $\Theta_i < 10$ molecules/cage, García-Sánchez et al.[1] report significantly higher $D_{i,self}$ values in ITQ-29 and LTA-Si using either flexible framework implementation, when compared to rigid framework simulations with the original crystalline structure. This is illustrated by the data presented in Figures 1a and b. For both ITQ-29 and LTA-Si, the diffusivities for both fixed and flexible frameworks have nearly the same values for loadings of $\Theta_i > 10$ molecules/cage. At these high loadings, the diffusion process is governed by intracage hops; flexibility issues are not of great importance. For LTA-5A, however, the Hill−Sauer flexible framework implementation gave results nearly the same as those for that the rigid framework over the entire range of loadings; see Figure 1c.

Commenting on their MD simulation results, García-Sánchez et al.[1] write "It is interesting to speculate if and why flexibility is essential to compute methane self-diffusivities". They further state that "none of the current force fields are able to capture the average structure exactly and specifically the 8-ring window separating the cages. A small deviation of the window from the crystal structure leads to very different diffusivities". The primary objective of this Comment is to quantify the influences of the chosen force field on the window dimensions. We shall demonstrate that the diffusivities are governed by the size of the 8-ring window aperture separating cages and that the size of the windows is influenced by the choice of the force field used to describe lattice flexibility. We aim to draw the unequivocal conclusion that lattice flexibility, per se, has no influence on the self-diffusivity of CH_4 in cage-type zeolites with 8-ring windows.

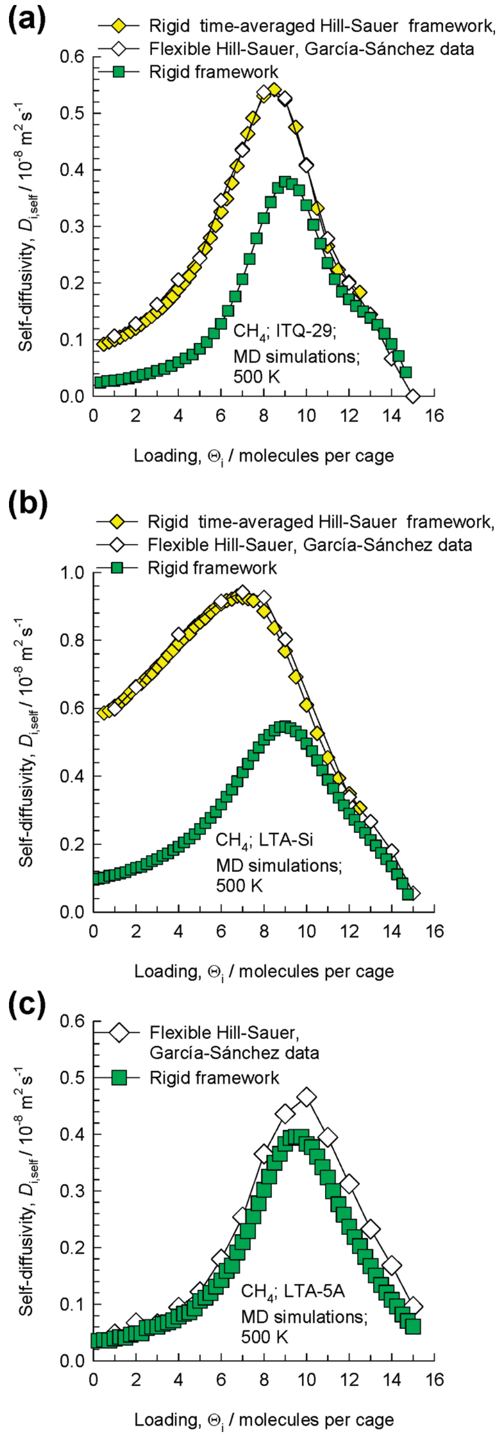

Figure 1. Comparison of rigid and flexible framework (with Hill−Sauer force field) simulations of the self-diffusivities, $D_{i,self}$, of CH_4 in (a) ITQ-29, (b) LTA-Si, and (c) LTA-5A. The data of García-Sánchez et al.[1] are plotted along with rigid framework simulations performed in this work, with both the original rigid crystalline framework and the time-averaged framework obtained from implementation of the Hill and Sauer[2] force field.

For a cage-type zeolite, two dimensions of the 8-ring windows of the original crystalline framework can be identified as indicated in Figure 2, (1) the shortest distance, d_{min}, and (2) the longest distance, d_{max}; these distances are also called straight and diagonal, respectively, in the work of Combariza et al.[4] The values of d_{min} and d_{max} are obtained by subtracting the van der Waals diameter of O atoms, taken to be equal to 2.7 Å, from the center-to-center distances of framework atoms in the 8-ring windows. The diameters determined following the method of Delaunay triangulation, described in the work by Foster et al.,[5] correspond with the

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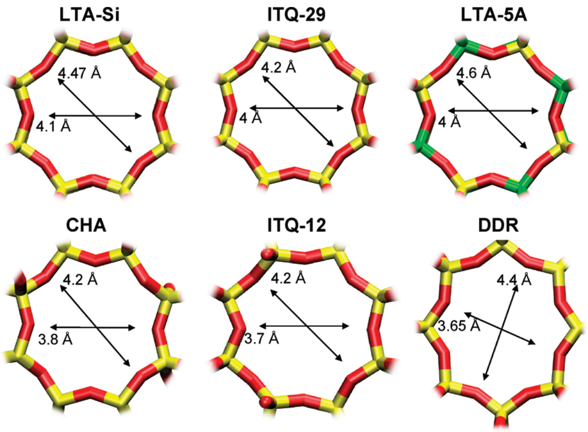

Figure 2. Window dimensions for cage-type zeolites with 8-ring windows. Two dimensions of the 8-ring windows are indicated, (1) the shortest (straight) distance, d_{min}, and (2) the longest (diagonal) distance, d_{max}.

d_{min} values; these also represent the maximum hard-sphere diameter that can pass through the 8-ring windows. The PFG NMR experiments of Hedin et al.[6] indicate a difference in the value of $D_{i,self}$ for CH_4 by 2 orders of magnitude when comparing DDR (d_{min} = 3.65 Å) and ITQ-29 (d_{min} = 4 Å).

We first investigated the lattice dynamics of the three frameworks using the Hill−Sauer[2] force fields. The lattice flexibility leads to a distribution of window sizes for (a) ITQ-29, (b) LTA-Si, and (c) LTA-5A; see Figure 3. Let us first consider the data in Figure 3a on window size distributions for ITQ-29; from these distributions, the values of the minimum and maximum window dimensions, determined from the time-averaged framework positions, are d_{min} = 4.04 Å and d_{max} = 4.56 Å. These values are both higher than the values of the original crystallographic framework, d_{min} = 4 Å and d_{max} = 4.2 Å. The larger values of the window dimensions obtained with the Hill−Sauer force field dictate the higher diffusivities at loadings of $\Theta_i < 10$ molecules per cage. To emphasize this, we performed MD simulations with a rigid framework using the time-averaged values of the framework atoms positions obtained from the Hill−Sauer force field implementation. These rigid framework simulations yield precisely the same diffusivity values as those obtained by García-Sánchez et al.[1] with a fully flexible framework; see the comparison of the two data sets in Figure 1a.

Let us now consider the data in Figure 3b on window size distributions for LTA-Si. From these distributions, the values of the minimum and maximum window dimensions, determined from the time-averaged framework positions, are d_{min} = 4.4 Å and d_{max} = 4.88 Å. These values are both significantly higher than the values of the original crystallographic framework, d_{min} = 4.1 Å and d_{max} = 4.47 Å. MD simulations with a rigid framework using the time-averaged positions of the Hill−Sauer implementation also yield precisely the same diffusivity values as those obtained by García-Sánchez et al.[1] with a fully flexible framework; see the comparison of the two data sets in Figure 1b.

The situation with respect to LTA-5A is somewhat different. The window size distributions with the Hill−Sauer force field yields d_{min} = 4 Å and d_{max} = 4.96 Å. Comparison with the corresponding values for the rigid framework, d_{min} = 4 Å and d_{max} = 4.6 Å, shows that the d_{min} value is practically unaltered. According to the work of Hedin et al.,[6] it is the d_{min} value that dictates the magnitudes of the $D_{i,self}$; we should therefore expect the Hill−Sauer flexible framework to yield the same diffusivities as for the rigid framework. This is indeed found to be the case in the data reported by García-Sánchez et al.;[1] see Figure 1c. Put another way, the rigid and flexible framework simulations (following Hill−Sauer) yield nearly the same results for LTA-5A because the d_{min} values remain practically unchanged.

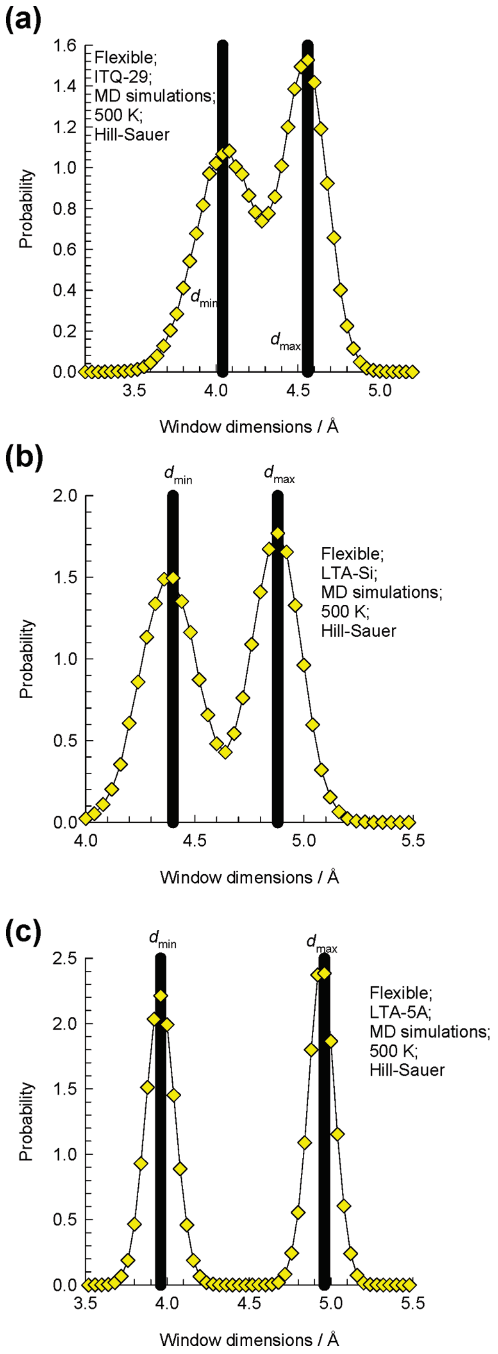

Figure 3. Distributions of window dimensions obtained for flexible framework dynamics of (a) ITQ-29, (b) LTA-Si, and (c) LTA-5A. The framework dynamics are obtained from MD simulations using the force field of Hill and Sauer.[2] These distributions are obtained without the presence of any guest molecules. Video animations of the lattice dynamics, obtained using the Hill−Sauer force field, are available as Supporting Information accompanying this publication.

For LTA-5A, García-Sánchez et al.[1] also report that the Nicholas et al.[3] force field yields a higher diffusivity value than that of the rigid framework; see Figure 4a. The window size

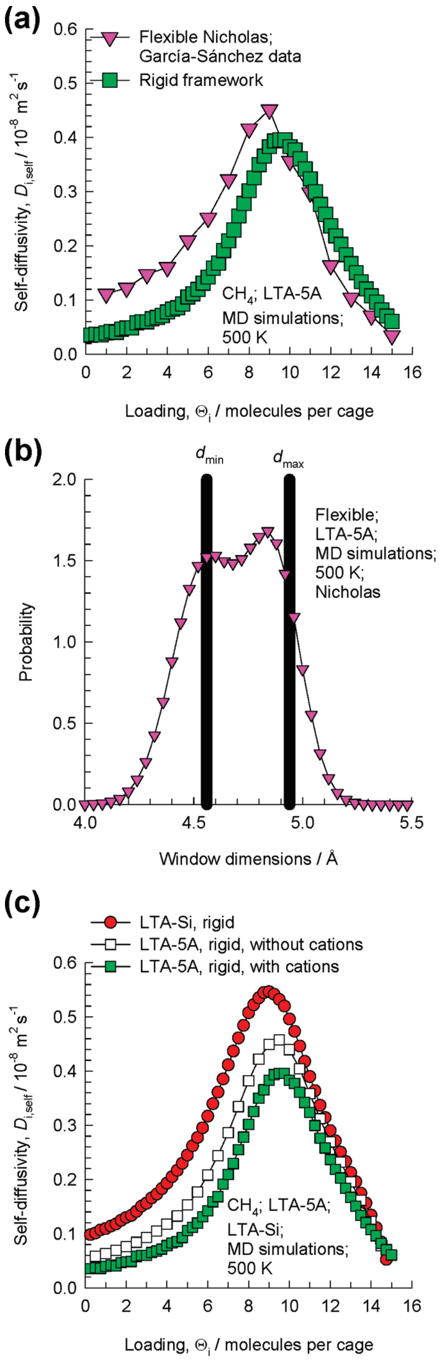

Figure 4. (a) Comparison of rigid and flexible framework (Nicholas et al.[3] force field) simulations of the self-diffusivities, $D_{i,self}$, of CH_4 in LTA-5A. (b) Distributions of window dimensions obtained for flexible framework dynamics of LTA-5A. The framework dynamics are obtained from MD simulations using the force field of Nicholas et al.[3] (c) MD simulations of the self-diffusivities, $D_{i,self}$, of CH_4 in LTA-Si and LTA-5A zeolites (all rigid frameworks) at 500 K as a function of the loading within the cages.

distributions of the lattice dynamics, portrayed in Figure 4b, yield $d_{min} = 4.56$ Å and $d_{max} = 4.94$ Å. The significantly higher value of d_{min}, obtained with the Nicholas implementation of lattice dynamics, is the reason for the higher values of $D_{i,self}$ of CH_4 in LTA-5A. The different $D_{i,self}$ values obtained with Hill−Sauer and Nicholas force fields can be explained in terms of significant differences in the d_{min} values; this explanation in terms of the differences in the d_{min} values is fundamentally different from the one offered by García-Sánchez et al.[1] These authors conclude that "the reverse behavior is essentially attributed to the interactions between the zeolite framework and the sodium and calcium cations".

The influence of the presence of cations on CH_4 diffusivities in LTA-5A needs further investigation. For this purpose, we compare in Figure 4c the $D_{i,self}$ data for a rigid framework of LTA-Si ($d_{min} = 4.1$ Å) with those for LTA-5A ($d_{min} = 4$ Å; Si/Al = 1; 4 Na^+ and 4 Ca^{2+} per cage). The diffusivities in LTA-5A are lower than those in LTA-Si for two separate reasons. To elucidate these reasons, we also carried out MD simulations using the LTA-5A framework, but without inclusion of any cations; the results are represented by the open square symbols in Figure 4c. The $D_{i,self}$ data for LTA-5A (without cations) lie below those of LTA-Si because of the lower d_{min} of the framework (see Figure 2); this result is in line with the data presented in Figure 4c. The $D_{i,self}$ data for LTA-5A (with cations) are also lower than those for the same framework in which the cations are excluded. The rationale is that the adsorption strength of CH_4 in LTA-5A is considerably higher due to the interactions with cations; this results in an increasing "sticking" tendency and a lower diffusivity, as explained in detail in our earlier work.[7]

In order to establish the generic validity of the conclusions that we wish to draw, we carried out flexible framework simulations using two additional force fields from the published literature; these force fields are those of van Beest et al.[8] and Pedone et al.[9] Figure 5 presents a comparison of rigid framework simulation results of the self-diffusivities of CH_4 in ITQ-29, LTA-Si, CHA, and ITQ-12 with those obtained for flexible frameworks obtained with the van Beest implementation. For ITQ-29 and ITQ-12, the rigid and flexible framework simulations yield practically the same $D_{i,self}$ values because the d_{min} of the time-averaged van Beest framework lattices is the same as that of the original crystal structures. Furthermore, the flexible framework simulation data coincide with those obtained from a rigid framework with the time-averaged framework obtained from implementation of the van Beest force field.

Analogous results to those presented in Figure 5 are obtained with the Pedone force field; see the Supporting Information for detailed information. For any given structure, the $D_{i,self}$ value obtained with a flexible framework simulation is dictated by the d_{min} value of the time-averaged positions of the framework atoms predicted by the chosen force field. This is illustrated in Figure 6a for ITQ-29, showing that the hierarchy of diffusivity values correlates with the corresponding d_{min} value. An analogous result holds for LTA-Si; see Figure 6b. The key role played by d_{min} is further emphasized in Figure 6c, which presents the values of $D_{i,self}$, determined at a pore concentration based on accessible pore volume $c_i = 1$ kmol m^{-3}, plotted as a function of the d_{min} of the corresponding rigid or flexible framework for a variety of cage-type zeolites with 8-ring windows. We note that an increase of 0.5 Å in the value of d_{min} results in an increase in the value of $D_{i,self}$ by about 2 orders of magnitude. The optimum choice of the window dimension is of importance in kinetic-based separations.[10,11]

The inescapable conclusion that emerges from our analysis is that the lattice flexibility, per se, has no influence on self-diffusivities in cage-type zeolites with 8-ring windows. The lattice dynamics derived from the Hill−Sauer, Nicholas, van Beest, and Pedone force fields do not always remain faithful to the original crystalline framework. Higher diffusivity values obtained from flexible framework simulations can be

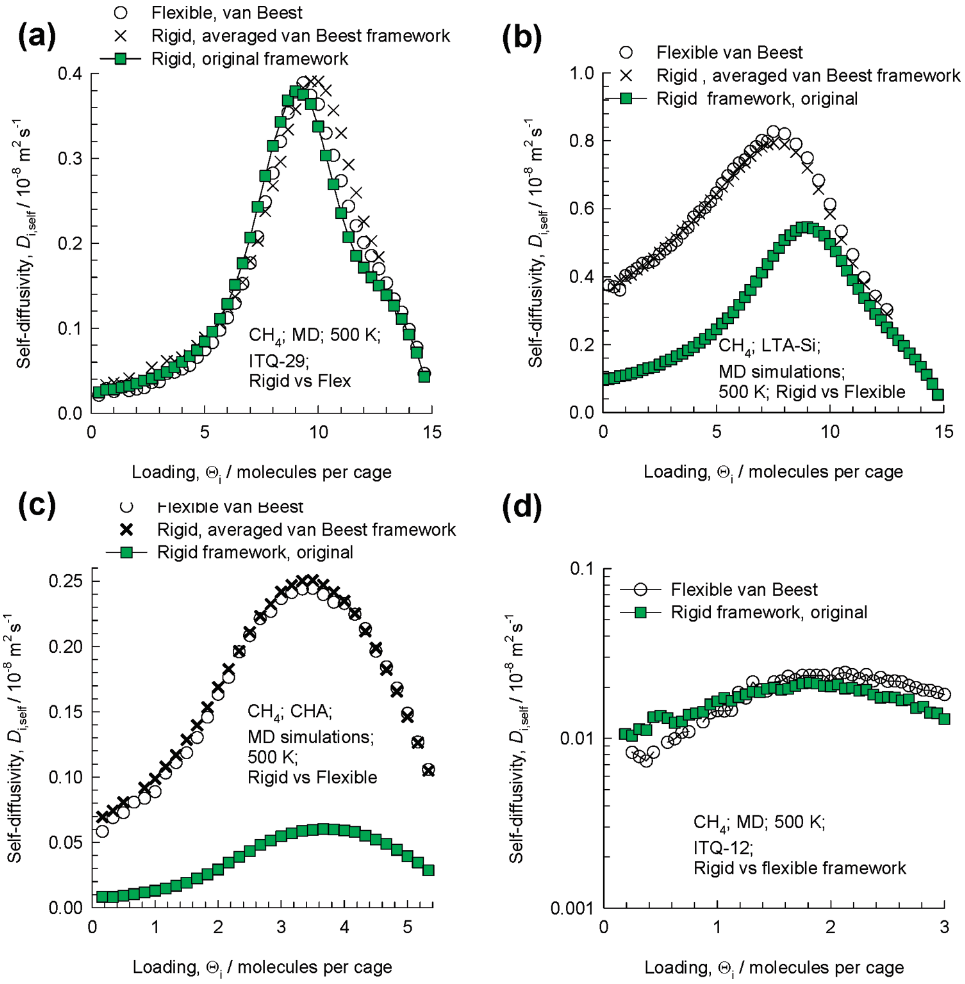

Figure 5. Comparison of rigid and flexible framework MD simulations (with the van Beest et al.[8] force field) of the self-diffusivities, $D_{i,self}$, of CH_4 in (a) ITQ-29, (b) LTA-Si, (c) CHA, and (d) ITQ-12 at 500 K. Also plotted are rigid framework simulation results obtained using the time-averaged framework obtained from implementation of the van Beest et al.[8] force field. Video animations of the lattice dynamics of CHA and ITQ-12 obtained with the van Beest et al.[8] force field are available as Supporting Information accompanying this publication.

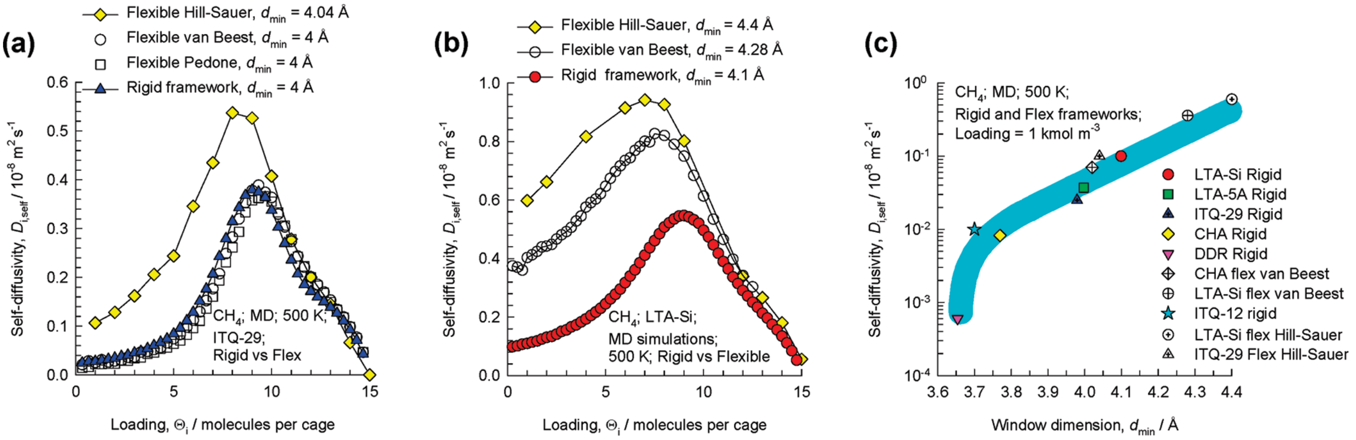

Figure 6. (a) Comparison of rigid and flexible framework MD simulations (van Beest, Pedone, Hill−Sauer force field implementations) of the self-diffusivities, $D_{i,self}$, of CH_4 in (a) ITQ-29 and (b) LTA-Si. (c) Values of $D_{i,self}$, determined at a pore concentration of $c_i = 1$ kmol m^{-3}, based on accessible pore volume, plotted as a function of the diameter d_{min}. The data for both rigid and flexible frameworks are included here. The flexible framework results correspond to those obtained with the van Beest force field.

rationalized in terms of larger d_{min} values of the time-averaged framework positions. Our conclusions are in complete agreement with those reached by Fritzsche et al.[12,13] for LTA zeolite. Our results also support the contention of Kopelevich and Chang[14] that lattice vibrations in zeolites cannot drive diffusion.

We conclude that in practice, it is not a requirement to perform MD simulations with flexible frameworks; rigid framework simulations are adequate.

Acknowledgment. R.K. acknowledges the grant of a TOP subsidy from The Netherlands Foundation for Fundamental

Research (NWO−CW) for intensification of reactors. The authors also acknowledge A. García-Sánchez for providing some simulation data files.

Supporting Information Available: The pore landscapes and structural details of the cage-type zeolites investigated in this article, along with force fields, simulation methods, and simulation results. Also available are animations showing the vibrations of the flexible lattices of cage-type zeolites. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP107956Z