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Unraveling the Argon Adsorption Processes in MFI-Type Zeolite

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The understanding of adsorption isotherms is important for the solution of a large class of industrial problems,
many of which are of current research interest. The existence of stepped adsorption isotherms is often observed
in some particular adsorption processes, being a distinction of mesoporous materials reflecting capillary
condensation effects. However, such singularity is less observed at very low relative pressures. For instance,
the presence of a substep on the argon adsorption isotherm of MFI at cryogenic temperature has been
corroborated with a variety of experimental studies, but its origin is still unclear, and the interpretations are
even contradictory. In this work, a new insight into this process is proposed by a combined approach using
both experiments and molecular simulations.

Attempts to understand physisorption phenomena of argon in MFI-type zeolite motivates a great deal of theoretical and experimental research.[1–8] MFI-type zeolite is of scientific and technological interest in heterogeneous catalysis, separation, purification, and lately in environmental applications.[9–11] This structure is characterized by two sets of interconnecting channels defined by 10-membered rings, with straight channels extending in the ⟨010⟩ direction and sinusoidal channels in the ⟨l00⟩ direction. It is well established by X-ray diffraction and NMR measurements that high-silica MFI undergoes a reversible phase transition at around 340 K, from a monoclinic to an orthorhombic structure.[12] The change in symmetry results only in minor changes of the framework positions and the unit cell vectors. Similar phase transitions from monoclinic to orthorhombic symmetry can also be reversibly induced by loading the zeolite with ammonia or with organic molecules.[13–15]

Argon adsorption isotherms at 77 K measured by several groups[16–20] all show a kink/step at around 23 argon atoms per unit cell. The origin of this substep remains a subject of debate. It has been considered as an argon transition from the fluid phase to a more crystalline commensurate phase,[19] as an intracrystalline process rather than a solidification occurring at the pore,[21] to adsorbent deformations,[22] and as a framework phase transition from the monoclinic to the orthorhombic symmetry.[6] We have combined experimental measurements with molecular simulations to provide new insights into the adsorption processes of argon in MFI at 77 K. Our goal was to establish the effect of

the adsorbate and the adsorbent on the nature and shape of the argon isotherm.

Adsorption studies were performed experimentally and using Monte Carlo (MC) simulations in the grand-canonical ensemble, and self-diffusion coefficients were obtained from the mean-square displacement using Molecular Dynamics (MD) simulations in the NVT ensemble and the velocity Verlet integration scheme with a time step of 0.5 fs. Simulations were performed for rigid (monoclinic,[23] $P2_1/n$ space group, and orthorhombic,[24] *Pnma* space group), structures of MFI and flexible frameworks. For the flexible zeolite, we used a model that includes bond stretching, bond bending, bond angle coupling, a dihedral potential, Lennard-Jones interactions, and electrostatic interactions.[25] The Ewald summation was used to handle electrostatic interactions. To validate this force field, we have computed the infrared spectra of the zeolite at 77 and 298 K, as well as the adsorption isotherm at 300 K, and compared the results with experiments.

Infrared spectra were obtained as the Fourier transform of the charge-weighted velocity autocorrelation function of the whole system.[26] The charges used are 1.1|e| for Si and −0.55|e| for O as provided by the model.[25] A step size of 1 cm^{-1} was chosen. Table 1 compares the peaks of the experimental spectra[27] with those obtained from molecular simulations at 77 and at 298 K. The agreement between the simulations and the experimental modes is excellent, thus validating the set of parameters used in this work for flexible structures. The modes between 1250 and 950 cm^{-1} correspond to strong bands attributed to the asymmetric Si−O stretching modes. The weak deformation modes between 820 and 650 cm^{-1} are assigned to a symmetrical Si−O stretching model, and those in the low-frequency region (650−400 cm^{-1}) are associated with Si−O−Si bending modes. Whereas the experimental spectrum exhibits

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TABLE 1: Infrared Spectra Peaks (cm^{-1}) Obtained from Molecular Simulations at 77 and 298 K and Compared with Experimental Spectra[27],[a]

experimental	MFI 298 K	MFI 77 K
444 (s)	464, 487 (w)	445, 480 (w)
552 (m)	562 (w)	560 (w)
804 (w)	770 (w)	776 (w)
1096 (s)	1102 (s)	1103 (s)

[a] The error bars in the computed frequencies are on the order of 10 cm^{-1} [(w) weak peak, (s) strong peak, (m) medium peak].
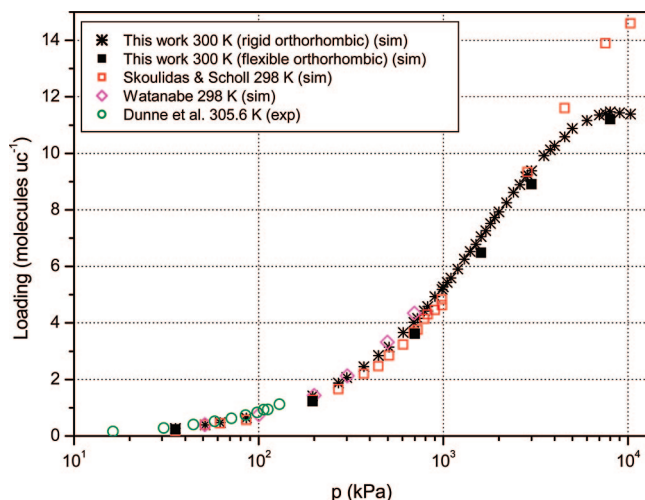
Figure 1. Computed adsorption isotherms of argon in orthorhombic MFI at 300 K using a rigid and a flexible framework, compared with available previous data.[25–27]

Figure 2. Experimental and computed adsorption isotherms of argon in MFI at 77 K.

broad but well-separated peaks at 444 and 552 cm^{-1}, computed MFI structures both at 77 and at 298 K exhibit an absorption range from approximately 380 to 560 cm^{-1} with many maxima. Only the most intense have been selected.

Figure 1 shows the computed adsorption isotherms of argon in orthorhombic MFI at 300 K and using a rigid and a flexible framework. The isotherms for a rigid and flexible framework are almost identical and in excellent agreement with available data.[28–30] The interactions of the adsorbed molecules with the zeolite are dominated by the dispersive forces between the guest atoms and the oxygen atoms of the zeolite,[31,32] meaning that the silicon van der Waals interactions are taken into account through an effective potential with only the oxygen atoms. Argon–argon Lennard-Jones interaction parameters were obtained by fitting the force field to the experimental vapor–liquid equilibrium curve using a truncated and shifted potential. Argon–oxygen Lennard-Jones parameters were obtained by calibrating the force field through explicitly fitting three points of the experimental isotherm shown in Figure 2. Simulations were performed at 2.0×10^{-3}, 9.0×10^{-2}, and 9.0×10^{-1} kPa using the rigid, monoclinic structure at 77 K. Detailed information about the force fields and simulation parameters can be found in the Supporting Information.

Low-temperature (77.3 K) and low-pressure experimental argon isotherms were measured in a Micromeritics ASAP 2010 M gas adsorption analyzer in the pressure range from 10^{-4} to 26 kPa. The instrument was equipped with a molecular drag vacuum pump and three different pressure transducers (0.133 kPa, uncertainty within 0.12% of reading; 1.33 and 133 kPa, uncertainty within 0.15% of reading) to enhance the sensitivity in the low-pressure range, which is especially useful in adsorption studies on highly microporous materials. Prior to the
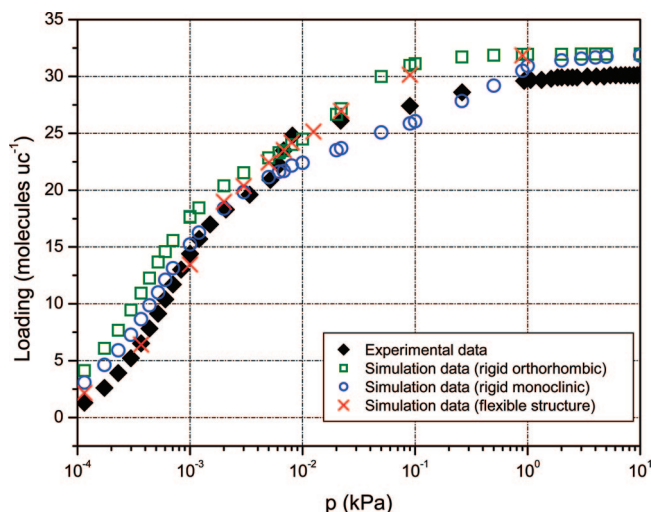
adsorption measurements, the sample was outgassed in situ under vacuum at 673 K overnight to remove any adsorbed impurities. The elapsed time for the measurement of the argon isotherm on silicate was 52 h, with over 100 equilibrium points. The argon saturation pressure was measured throughout the entire analysis by means of a pressure transducer; the nonideality factor was 5×10^{-5}. Argon was supplied by Air Products with an ultrahigh purity (i.e., 99.9992%).

Figure 2 shows the experimental and computed adsorption isotherms of argon in MFI at 77 K. Simulations were performed for (a) the crystallographic monoclinic and orthorhombic structure, keeping the framework rigid during the simulation and (b) a flexible framework starting from the monoclinic structure. The experimental adsorption isotherm obtained for argon is of type-I character, although it exhibits a substep at 5 $\times 10^{-3}$ Pa, in agreement with those found previously in the literature.[16–20] Our simulation results using rigid frameworks correctly reproduce the saturation loading (simulations always provide slightly higher saturation loadings than experiments since the simulated frameworks are defect free), but they underestimate adsorption in the monoclinic structure and overestimate adsorption in the orthorhombic structure, in the vicinity of the substep region. Furthermore, both overestimate the adsorption in the low-pressure regime. On the other hand, the simulation data using the flexible framework show good agreement with the experimental isotherm in the whole range of pressures, matching closely with those obtained for the rigid monoclinic framework at low pressures and with those obtained for the rigid orthorhombic framework at high pressures.

Additional Molecular Dynamics simulations have been performed to compute self-diffusion coefficients for 7, 14, 23, and 31 molecules of argon per unit cell at 77 K in rigid and flexible frameworks. The obtained results are listed in Table 2. Diffusion decreases with argon loading and shows lower values for the orthorhombic structure than those for the monoclinic structure. Simulations using a flexible framework show intermediate self-diffusion coefficients for 7, 14, and 23 molecules of argon per unit cell and an increased diffusivity at the saturation loading. The fact that simulations using flexibile frameworks provide adsorption and diffusion values between those obtained for the rigid structures suggests a monoclinic to orthorhombic transition and not a phase transition of argon due to the confinement as the most probable reason for the adsorption substep; that would provide much lower diffusion

TABLE 2: Computed Self-Diffusion Coefficients in MFI-Type Zeolite As a Function of Argon Loading at 77 K

molecules of argon per unit cell	$D \ 10^{-11}$ $[m^2 \ s^{-1}]$ monoclinic rigid structure	$D \ 10^{-11}$ $[m^2 \ s^{-1}]$ orthorhombic rigid structure	$D \ 10^{-11}$ $[m^2 \ s^{-1}]$ flexible structure
7	34 ± 2	30 ± 3	32 ± 5
14	29.1 ± 1.5	22.5 ± 0.5	26.2 ± 1.0
23	8.1 ± 1.5	7.8 ± 1.1	8.0 ± 1.6
31	0.39 ± 0.12	0.7 ± 0.3	0.7 ± 0.4

coefficients in the substep than the ones obtained from our calculations. In general, an increase in adsorption in the zeolitic pore provokes a decrease in the molecular diffusion. The experimentally pronounced kink implies a fast adsorption in a very narrow pressure range and therefore a decrease in the diffusion coefficient. If this "fast" adsorption was also affected by a phase transition of the argon, the molecular order would be higher, leading to an even lower molecular diffusion.

Molecular simulations starting from the monoclinic framework but allowing framework flexibility provide indirect evidence of the framework change upon argon adsorption with (1) values for the self-diffusion coefficients completely comparable with those obtained from the rigid structures, (2) good agreement with the experimental adsorption isotherm at 77 K in the whole range of pressures, as shown in Figure 2, and (3) strongly increasing framework–framework interactions when the loading of argon is increased, indicating deformations of the framework (Figure 3a). Argon–argon and argon–framework energies obtained at several pressures and at the substep show no evidence of a phase transition of argon following a quasi-linear behavior of the energy with argon loading (Figure 3b).

According to our simulations results, the favorable adsorption sites for argon are the straight channels at very low loadings

(less than 2 molecules per unit cell), but the molecules are pulled off of those sites toward the zigzag channels at medium coverage (16 molecules per unit cell). Argon molecules completely fill the pore intersections at saturation once the zigzag and the straight channels are full. Our findings are in agreement with those proposed in 1994 by Pellenq and Nicholson.[33] They provided a similar mechanism for the filling of the MFI pores and suggested a change in the framework as the most plausible explanation for the experimental substep at 23 molecules per unit cell at 77 K, but none of their models were able to reproduce it. We have presented a combination of high-quality experiments and molecular simulations that provide additional support that a subtle interplay between the guest molecules and the flexible host structure could be responsible for kinks/steps in the isotherms.

Supporting Information Available: (a) The functional form of the force field for flexible MFI-type zeolite and for argon in MFI-type zeolite, (b) the vapor–liquid equilibrium curve of Ar showing experimental and simulated data, (c) the energy profiles obtained directly from our simulations during argon adsorption at 77 K and 5×0^{-3} kPa, and (d) the movie showing the changes observed in the monoclinic, flexible structure of MFI with increasing loading of Ar. This material is available free of charge via the Internet at http://pubs.acs.org.
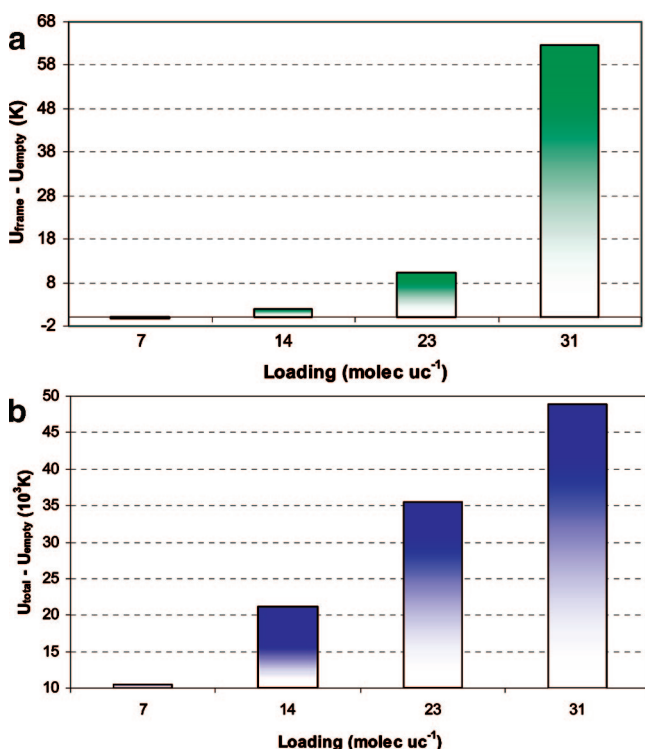
Figure 3. Computed interactions as a function of argon loading at 77 K normalized versus the energy of the empty framework (U_{empty}); (a) framework–framework interactions (U_{frame}) and (b) framework–framework, framework–argon, and argon–argon interactions (U_{total}). The energy for the empty framework U_{empty} is 1.04276610×10^8 K

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