Transferable force field for modelling of CO$_2$, N$_2$, O$_2$ and Ar in all silica and Na$^+$ exchanged zeolites.

Supplementary Information

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1 Liquid-vapor coexistence for gas models used in this work

Here we present computed liquid-vapor coexistence curves for several different gases and gas models. Besides gas models of CO$_2$, N$_2$, O$_2$ and Ar used in this work, we also compare several other models for CO$_2$ and N$_2$, frequently used in the literature. Agreement between experimental and simulation data is good for most of models which to a certain degree validates a choice of the used models.
Figure S1: Comparison between experimental and simulated coexistence curves for three CO₂ models. EPM2 model is used as the main model in this work, EP model from ref.¹ and TraPPE model from ref.² Experimental data downloaded from NIST database.³
Figure S2: Comparison between experimental and simulated coexistence curves for two N$_2$ models. Experimental data downloaded from NIST database$^{33}$ and force field parameters from ref$^{3}$ for the 3-site model (used in the manuscript) and for a two-site "2LJ.BP" model from ref$^4$.

Figure S3: Comparison between experimental and simulated coexistence curves for argon and oxygen. Experimental data downloaded from NIST database$^{33}$ For force field parameters for Ar$^6$ and O$_2$ $^{7,8}$ are the same as in the main article.
2 Comparison between adsorption in FAU zeolite using rigid and flexible EMP2 model of CO$_2$

Figure S4 shows comparison between adsorption loadings computed using rigid and flexible EPM2 models for CO$_2$ molecule. The simulations were performed using RASPA$^{9-11}$ code. During the GCMC simulation, sodium ions were allowed to move.

![Figure S4: Comparison between computed adsorption isotherms at 273 K with flexible and rigid EPM2 models for CO$_2$ molecules in FAU zeolite framework with Si:Al = 1.40. Experimental data taken from the work of A. Farid and L. Bergström.][12]
3 Adsorption computed with different CO$_2$ models: EP, EPM2, TraPPE

In principle any of the considered models (EP, EPM2 and TraPPE) could be used for the force field optimization, since all the models reproduce well the liquid-vapor coexistence curves (Fig. S1). Still, EPM2 model is known for being able to reproduce better a critical region of liquid-vapour coexistence curve as well it provides correct quadrupole moment of CO$_2$ molecule.

In this particular example we compare the performance of the three CO$_2$ models for adsorption of pure CO$_2$ gas in LTA zeolite with Si:Al=5 for four different temperatures. In all cases EP and EPM2 models shows very similar results, while TraPPE model yields a higher adsorption. Similar trends of adsorption of these three models can be obtained for other structures and Si:Al ratios. The force field parameters developed in this work for interaction between zeolite framework and CO$_2$ molecules are optimized on the basis of the EPM2 model, and provide balanced description of adsorption across different zeolite frameworks. We can therefore expect that EP model would provide similar performance in description of adsorption of different zeolites if used with developed in this work force field, while TraPPE model may in average overestimate adsorption.
Figure S5: Comparison of adsorption performance for three CO$_2$ models, EP, TraPPE and EPM2 in LTA zeolite with Si:Al=5. Experimental data for temperature 303K are taken from Palomino et al.
4 N$_2$ adsorption using three- and two-site N$_2$ models

In Fig. S2 we have demonstrated that both two-site and 3-site models for nitrogen molecule are able to reproduce experimental liquid-vapor coexistence curve. However, adsorption behaviour of these models is different. In case of all-silica FER zeolite (Fig. S6) performance of the three-site model is good while two-site model somewhat underestimate adsorption. In case of cation exchanged zeolites, the two-site model highly underestimate adsorption. This can be understood since in Na$^+$-exchanged zeolites the gradient of the electric field is stronger than in all-silica zeolites due to presence of counterions and more negative net charge of the framework, and the quadropole moment of the 3-site model, interacting with this inhomogeneous electric field, provides stronger adsorption which is more consistent with the experimental results.

![Figure S6: Comparison between experimental and simulated adsorption isotherms of pure N$_2$ gas in all silica FER zeolite at 303K. Two nitrogen models, with 2 sites and 3 sites (the main model used in this work) were compared. Experimental data for comparison are taken from T.D. Pham et al.][1]
Figure S7: Comparison between experimental and simulated adsorption isotherms of pure N$_2$ gas in FAU zeolite with Si:Al = 1.00, at 293, 303 and 313K. Two nitrogen models, with 2 sites and 3 sites (the main model used in this work) were compared. Experimental data for comparison are taken from Park et al. Yellow coloured area stands for the difference between adsorption loading of 3 and 2 sites N$_2$ models.
Comparison between CO$_2$ adsorption in free and blocked sodalite cages in LTA type zeolite

Many zeolite frameworks have sodalite cages formed by 4- and 6-members rings not penetrable by small gas molecules. An example is shown in Fig. S8 indicating positions of the sodalite cages within LTA zeolite framework. These cages are normally not accessible to adsorption from outside the framework. Since in the Grand Canonical Monte Carlo a guest molecule can be inserted in any place in the simulation box, it may in principle occasionally appear inside such cage making artificial increase of the adsorption load. In order to exclude such possibilities, sodalite cages should be blocked in CGMC simulations.

Figure S8: Sodalite cages inside of LTA zeolite framework with Si:Al ratio equal to 1. Standard position is indicated with the violet spheres. Figure taken as a snapshot from GCMC simulation of adsorption in rigid zeolite framework and movable sodium cations. For clarity reasons sodium ions are omitted. Simulation performed using code RASPA,$^{9,11}$ and actual figure created using Materials Studio 7.0.$^{10,17}$
Figure S9: FAU zeolite with Si:Al ratio of 1.40. Sodium cations and blocking spheres are for clarity omitted. Yellow part represent accessible volume for CO$_2$ molecules.

Figure S10: FAU zeolite structure with Si:Al ratio of 1.23, loaded with CO$_2$ molecules. For clarity reasons zeolite is presented as all silica structure, sodium ions and blocking spheres are omitted. Green "stars" stands for position of blocking pseudo atoms. Figure taken from the output of CO$_2$ adsorption at pressure and temperature of 100 kPa and 253K respectively, corresponding to conditions close to saturation. During the simulation sodium ions were allowed to move while blocking pseudo atoms were positionally restrained to their original coordinates.
We blocked sodalite cages with dummy LJ sites ($\sigma = 3.50\text{Å}$) utilizing code for identification of Composite Building Units in zeolite structures. Results were in agreement with *zeo++* code based on *Voronoi* network. Only interactions between blocking sites and guest molecules via hard-sphere potential were taken into account, while interactions between framework atoms (as well as Na+) and blocking sites were ignored. The hard-sphere potential is given as follows

$$U_{ij}^{\text{vdW}} = \begin{cases} +\infty & \text{if } r_{ij} \leq r_c \\ 0 & \text{otherwise} \end{cases}$$

where $r_c$ equal to 3.50Å.

In order to check the importance of blocking, we have compared adsorption isotherms for LTA-type zeolite with blocked and with free sodalite cages. The results are presented in Fig. S11.

![Figure S11: Comparison between computed adsorption isotherms at 303 K with free (blue) and blocked (red) sodalite cages in LTA zeolite with Si:Al = 3.5.](image)

Adsorption data obtained for Si:Al = 3.5 and pure silica LTA zeolite show only a small difference between the adsorption load. Note that our force field, in contrast to most of other
force fields in the literature, has non-zero Lennard-Jones parameters assigned to Si and Al atom, which may reduce free volume in sodalite cages available for guest molecules.

6 Adsorption in zeolite framework with fixed and free Na\(^+\) ions

To demonstrate effects of the framework cations mobility onto adsorption of the CO\(_2\), we compare adsorption isotherms computed in LTA (Fig. S12) and FAU (Fig. S13) zeolites with rigid (fixed) and flexible (free) sodium cations.

Figure S12: Computed adsorption isotherms in LTA zeolite with fixed (blue) and free (red) Na\(^+\) ions.

In the case of LTA zeolite, the average difference between adsorption loadings obtained for fixed and free sodium ions was around 2%. For FAU zeolite, this difference was even smaller, around 1%. The results indicate that the mobility of the sodium ions is not affecting adsorption loadings in a noticeable way.
Figure S13: Computed adsorption isotherms in FAU zeolite with fixed (blue) and free (red) Na\(^+\) ions.

7 Comparison between CO\(_2\) adsorption in rigid and flexible zeolite framework

In order to check importance of the zeolite framework flexibility on the adsorption properties we compared (Fig. S14 and Fig. S15) adsorption isotherms of CO\(_2\) in two commonly used FAU and LTA zeolites with flexible and rigid framework. In both examples Na\(^+\) ions were treated as movable with associated translational moves. Framework flexibility was reached by translation steps of randomly chosen framework atoms (one at a time) with small displacement from the original atomic position. The difference between two isotherms in each example is within marker size and within the statistical uncertainly. However, considering zeolite framework as flexible leads to increases of the CPU time needed for simulation.
Figure S14: Comparison between computed adsorption isotherms at 273 K with flexible and rigid FAU zeolite framework with Si:Al = 1.40.

Figure S15: Comparison between computed adsorption isotherms at 303 K with flexible and rigid LTA zeolite framework with Si:Al = 3.5.
8 CO₂ adsorption in LTA zeolite with 1:1 Si/Al ratio

Figure S16 shows comparison between experimental and computed adsorption isotherms in LTA type zeolite with Si:Al ratio equal to 1 in the logarithmic scale. Also shown is result of a force field described in the same work by Martin-Calvo et al. The later shows a better agreement with the experimental curve, but it should be noted that in the force field from work partial atom charges were specially fitted to reproduce adsorption curve for this zeolite.

Figure S16: Comparison between experimental, computed with force field from ref. and computed in this work, adsorption isotherms of pure CO₂ in LTA type zeolite with Si:Al = 1.00, at 273 and 298 K. Experimental data and simulated data with force field from ref. are reproduced from the work of Martin-Calvo et al.
Comparison between computed in this work and previously reported adsorption isotherms of CO$_2$ in MFI (ZSM-5) zeolite

It was suggested in a number previous studies$^{22,23}$ to introduce a partial charge transfer on Na$^+$ cations in order to describe experimental adsorption isotherms. In the present force field we keep the charge of Na$^+$ cations equal to 1.0\(e\). Here we compare results obtained within our force field with work of Newsome et al.,$^{22}$ where the authors include partial charge transfer on given cation. They evaluate three partial charges on Na$^+$ cations, equal to 1.0, 0.7 and 0.4 \(e\), and the best agreement with experimental data was found to be for partial charge of 0.7 \(e\). Fig. S17 shows that our result is very close to result by Newsome et al.$^{22}$ corresponding to Na$^+$ cation charge 0.7 \(e\) which by the authors of that paper was defined as optimal for adsorption studies.

Figure S17: Comparison of CO$_2$ adsorption in MFI zeolite with Si:Al=13 at 308K. Experimental data, and data from previous simulation are taken from the work of Newsome et al.$^{22}$
N\textsubscript{2} adsorption computed with original and re-optimized parameters for nitrogen

Results for nitrogen adsorption presented in the main text in Figs. ?? and ?? were computed with the original force field parameters for N\textsubscript{2} molecule from ref\textsuperscript{13} and showed a trend to underestimate the adsorption load. We found that relatively small re-optimization of the Lennard-Jones parameters for nitrogen results in clear improvement of the agreement with available experimental data. These re-optimized force field parameters for N\textsubscript{2} are given as follows:

\[ \varepsilon(\text{N}_n2) = 40.24 \text{ K} \]

\[ \sigma(\text{N}_n2) = 3.32 \text{ Å} \]

\[ q(\text{N}_n2) = -0.482 \text{ e} \]

\[ q(\text{N}_\text{mid}) = 0.964 \text{ e} \]

Note that only Lennard-Jones parameter \( \varepsilon \) was changed.

Fig. S18 – S20 show comparison of nitrogen adsorption isotherms between experimental and computed with optimized N\textsubscript{2} parameters given above. One can see that for all-silica FER, CHA, MFI and STT zeolites of Fig. S18 simulation results somewhat overestimate adsorption. For FAU and MFI structures (Fig. S19 and S20) simulation results slightly underestimate adsorption but show clear improvements compared to simulated results with N\textsubscript{2} parameters from ref\textsuperscript{26} shown in Fig. ??–b and Fig.?? of the main text. Overall, the agreement with experimental N\textsubscript{2} adsorption isotherms become better and updated parameters may be more reliable in prediction of nitrogen adsorption in zeolites at ambient temperatures. Note however that change of N\textsubscript{2} parameters may change behaviour of nitrogen at low temperature around transition to the liquid phase. Also, because of a limited number of available nitrogen adsorption isotherms measured at ambient temperatures, given in this paper nitrogen force field parameters may need further adjustment.
Figure S18: Comparison of experimental and simulated with re-optimized parameters, adsorption isotherms of pure N₂ in: FER, CHA, MFI and STT all silica zeolites at 303 K. Experimental data for comparison are taken from T.D. Pham et al.\textsuperscript{14}

Figure S19: Comparison between experimental adsorption isotherms and those obtained with the reoptimized FF (this work). Experimental data for comparison are taken from Dunne et al.\textsuperscript{27} for FAU (NaX) with Si:Al equal to 1.23 and MFI with Si:Al = 30, and Jayaraman et al.\textsuperscript{28} for FAU (NaX) with Si:Al = 1.25.
Figure S20: Comparison between experimental adsorption isotherms and those obtained with optimized force field (this work), for FAU zeolite with Si:Al ratio equal to 1. Experimental data for comparison are taken from Park et al.¹⁵
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