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Title: Adsorption of CO_2-C_3H_8 mixtures on Na-ZSM-5: a molecular simulation study

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Abstract: Zeolite crystals with cations present, such as Na-ZSM-5, are widely used for gas sequestration, and separation process.One possible application is as an adsorbent to separate CO_2 from propane (C_3H_8) in petrochemical industry. This separation by zeolites is a defying research topic, because there are size and polarizability differences between the molecules. In literature, it is reported experimentally inverse shape selectivity in adsorption of this mixture on Na-ZSM-5 [1].

In this work, molecular simulations (GCMC) were performed to evaluate the equilibrium of adsorption of CO_2/C_3H_8 pure and binary mixtures on Na-ZSM-5 zeolite.

The crystalline structure of Na-ZSM-5 was built by replacing Si atoms with Al atoms (obeying Lowenstein's rule) starting from an all-silica zeolite structure (silicalite-1) obtained in the literature [2]. The Si/Al ratios desired were 15 and 60. The cations Na^+ were inserted on the structure by canonic (NVT) simulations. The parameters used to represent the oxygen on the rigid framewok was found on the work of June, Bell and Theodorou [3] and Makrodimitris et al.[4] and the parameters associated to the Na^+ were based on Calero work [5].

In order to carry out the simulations, we identified in the literature suitable models for describing the gases in the bulk phase. CO_2 molecule was treated by a three site rigid model (TraPPE[6]) that account the intrinsic quadrupole moment using partial charges. For the C_3H_8, the TraPPE model [7] already was select, in which the molecules are treated by a discharged united atom representation.

The potential energies associate with different sites were tuned aiming to represent experimental equilibrium isotherms.

Non-bonded interactions $U(r_{ij})$ are modeled using pairwise-additive potentials consisting of Lennard-Jones (LJ) 12-6 and Coulomb's law [8]:

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}}$$

During the development of the work, we tested the influence of partial charges of the extraframework cations on the correct representation of experimental data. Comparing the adsorption of CO_2 on silicalite-1 and Na-ZSM-5 (both zeolites have MFI framework), it is clear the electric field created by the sodium cation distribution strongly increase the adsorption of the CO_2.

Our results showed that the force field presented depicts well the isotherms studied. The magnitude of the potential energies associated with different sites on cationic zeolite suggest there are a polarization effect on propane when these molecules are in mixtures with CO_2 on Na-ZSM-5.

Key-words: Adsorption, GCMC, separation, ZSM-5
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