

Adsorptive-based recovery of bioalcohols: A simulation and experimental study

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Due to rising fossil fuel prices and associated environmental issues, renewable energy has received increasing global interest. Currently, bio-alcohols, especially ethanol and butanol, are considered to be sustainable alternatives to fossil fuels.[1] They are useful both as a biofuel and as an additive to gasoline to improve its quality due to their high octane rating. Bioethanol and other biofuels produced during biomass conversion must be separated from the fermentation broth before being used as a fuel, which is challenging. Since the biofuel products are typically dilute alcohol-in-water solutions, an energy efficient alcohol-water separation technology is required to generate fuel-grade alcohols. At such a low concentration of solvents, the energy required for the separation by traditional distillation is higher than the energy content of the product itself. To achieve a more energy-efficient alcohol recovery, a number of removal techniques have been investigated including adsorption, gas stripping, pervaporation or reverse osmosis.

In this work we focused on adsorptive-based recovery. Silicalite-1 or ZSM-5 zeolite (MFI topology) is likely the material most often used to this end. Its channel-like topology and hydrophobic properties can selectively adsorb small organic molecules like C1-C4 alcohols from dilute aqueous solutions. Despite the similarity with silicalite-1, silicalite-2 or ZSM-11 (MEL topology) has been scarcely studied for this separation. The main difference between both structures is that whereas in MFI zeolite zig-zag channels connect the cavities, the channels are linear in MEL (see Fig. 1).

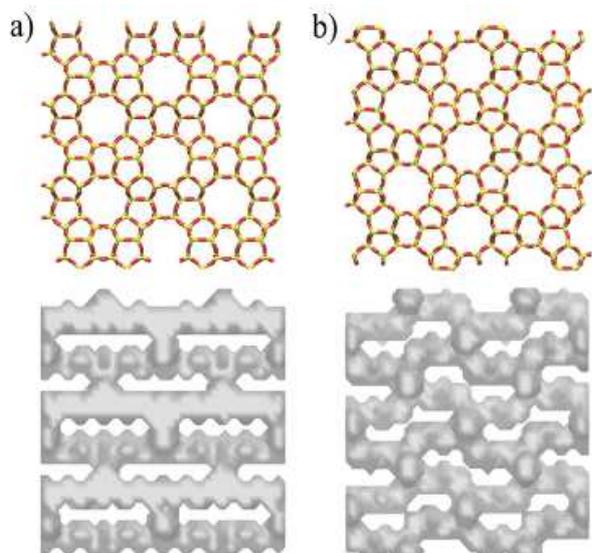


Figure 1: Atomic structure and accessible solvent surface of a) MEL and b) MFI zeolites.

Although the separation process by exploiting the preferential equilibrated uptakes is expected to be similar in both structures, kinetically driven separations can be notably sensitive to subtle structural differences. The unary adsorption isotherms of the compounds of interest, water and C1, C2 and C4 alcohols, were obtained from both experiments and molecular simulations. The measurements were carried out on a stainless steel volumetric apparatus with a pressure transducer (Pfeiffer Vacuum, APR 266) and equipped with a vacuum system that allows a vacuum better than 10^{-2} Pa. Details of the synthesis of the ZSM-11(Si) sample are reported elsewhere.[2] Experimental adsorption data on multicomponent mixtures are however difficult to address, and hence the molecular simulation (MS) technique represents a fundamental tool in this context. We computationally obtained the adsorption isotherms of alcohol/water binary mixtures via Grand Canonical Monte Carlo (GCMC) simulations using RASPA code [3] and those models and force fields showing the best agreement with experiments. To account for diffusion behaviours, we performed Molecular Dynamics (MD) simulations using LAMMPS software package. The force fields employed in the GCMC simulations were also used in the MD simulations for consistency. The initial configurations for MD simulation were taken from the equilibrated configurations of previous GCMC simulations. The MD simulations were performed in the *NVT* ensemble using Nose-Hoover thermostat [4] to fix the temperature.

Since the underlying adsorption mechanisms are generally difficult or impossible to be determined by experiments, especially in the case of mixtures, MS becomes again essential. We conducted a comprehensive microscopic analysis in terms of energetic and structural factors, such as radial distribution functions, hydrogen bonding and occupation profiles. Finally, it is worth noting that the study was carried out at 298 K and 323 K to assess the effect of the temperature on the adsorptive separation and the involved microscopic processes, which is of interest from industrial and fundamental viewpoints, respectively.

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