Selectivities for binary mixtures of hydrogen/methane and hydrogen/carbon dioxide in silicalite and ETS-10 by Grand Canonical Monte Carlo techniques

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Abstract

Current environmental problems have created the need to search for cleaner fuels. Hydrogen has been proposed as a clean fuel because its combustion by-product is water. Unfortunately, hydrogen is not readily available in pure form. It is obtained from steam reforming ($CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$) and dry reforming ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$) [1] and has to be separated from methane, carbon dioxide and smaller amounts of other gases before the hydrogen can be used effectively in a fuel cell [2]. Current hydrogen separation membranes are made of palladium alloys or chemically and mechanically unstable organic polymer membranes [3]. Palladium membranes are costly and in limited supply. The use of zeolites and titanosilicate molecular sieves creates stable inorganic matrices and consequently stable membranes [3]. These nanoporous materials can be made into membranes that have the potential to separate hydrogen from methane.

In this study the separation capabilities of silicalite and the titanosilicate molecular sieve ETS-10 for binary mixtures of hydrogen/methane and hydrogen/carbon dioxide were evaluated by equilibrium molecular simulation techniques. This is the first molecular simulation study that presents mixture adsorption isotherms of these components in silicalite and ETS-10, and determines selectivities based on the simulation results.

Grand Canonical Monte Carlo (GCMC) simulations were carried out for pure components and binary mixtures for hydrogen/carbon dioxide and hydrogen/methane at 298K to determine pure and mixture adsorption isotherms. The pure and mixture adsorption isotherms were calculated up to pressures of approximately 2000 bar. The results of this study indicate that the separation of hydrogen from methane or from carbon dioxide in silicalite would be successful, since hydrogen in a 50% bulk mixture does not adsorb unless the pressure is very high, on the order of 500 bar.

In contrast, in ETS-10, hydrogen in a 50% bulk mixture adsorbs at a pressure near 10 bar. Simulations of adsorption in ETS-10 showat low, intermediate and high pressures a higher selectivity for the separation of carbon dioxide from hydrogen than the separation of methane from hydrogen. Simulations of adsorption in silicalite show a higher selectivity for the separation of carbon dioxide from hydrogen than the methane/hydrogen separation at high pressures only. Analysis of isosteric heat of adsorption information indicates that silicalite is energetically homogeneous with the adsorbates.

In contrast, ETS-10 has energetic heterogeneity, as shown by the decrease of the heat of adsorption with increasing loading.

References

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