

# Packing induced selectivity effects in the liquid phase adsorption of Alkane/Alkene/Aromatic mixtures on FAU-type Zeolites

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## Abstract

In this work, the liquid phase adsorption of hydrocarbons on large cage faujasite type zeolites is studied. The used hydrocarbons are alkanes (C<sub>5</sub>-C<sub>14</sub>), alkenes (C<sub>6</sub>-C<sub>12</sub>) and aromatics (C<sub>6</sub>-C<sub>9</sub>). Special attention is devoted to molecular packing mechanisms that influence the selectivity and maximum adsorption capacity of alkenes and aromatics.

Adsorption in liquid phase is typically influenced by non-idealities like adsorbate-adsorbate interactions and packing effects that can overrule adsorbate-adsorbent energetic interactions. In first instance, the energetic effects are studied by performing gas chromatographic pulse experiments at very low coverage. The zero coverage adsorption enthalpy of alkanes and aromatics is found to increase linearly with the carbon number, as does the adsorption entropy.

The influence of faujasite characteristics (Si:Al-ratio and cation size) on the adsorption of alkanes (C<sub>6</sub>-C<sub>8</sub>) and benzene is studied. Surprisingly the Si:Al-ratio of NaY zeolites has no influence on the adsorption enthalpy of alkanes and aromatics. Only when going from NaY to NaX, a significant increase of the interaction energy is observed. When exchanging the Na cations for bigger Cs cations, the interaction energy for alkanes and aromatics significantly increases.

Both alkenes and aromatics are stronger adsorbed compared to alkanes. The presence of a double bond inside C<sub>4</sub> molecules leads to an increased adsorption enthalpy of more than 11kJ/mol on NaY, while the aromatic ring causes an increase between 12.5 and 21.8 kJ/mol, depending on the zeolite characteristics.

Before studying the liquid phase adsorption of hydrocarbons on faujasites, a lot of effort was devoted to a careful validation of a variety of experimental techniques. The liquid phase pulse chromatographic technique appears to be inapplicable because the presence of water in the carrier inevitably leads to the degeneration of the faujasites containing a large amount of aluminum. The influence of water, leading to erroneous results, is avoided by application of a batch experimental technique, during which only a limited amount of liquid is added to the zeolite. The batch adsorption technique is used to study the adsorption of alkene/alkene, alkane/aromatic and alkene/aromatic mixtures at room temperature. Under these experimental conditions, the faujasite's micropores are completely saturated with hydrocarbons, which distinguishes the experiments from gas phase measurements.

Chain length induced selectivity effects are observed in the adsorption of alkene/alkane mixtures on NaY (Si:Al 2.79). Adsorption isotherms of alkenes having different chain lengths (hexene, octene, decene, dodecene) from hexane, heptane, octane, decane, dodecane and tetradecane solvents are measured. Already at low concentrations, the alkenes are selectively adsorbed from their binary mixture with an alkane. Within the investigated alkene concentration range, between 0 mol% and 20 mol%, only for hexene the maximum adsorption capacity of 0.32 ml/g, corresponding to 25 hexene C-atoms per supercage is reached. The amount alkene adsorbed depends on the chain length of both the alkene and the alkane. Two remarkable effects are observed: (1) shorter alkenes are preferentially adsorbed compared to longer alkenes, (2) the adsorption of the alkene depends strongly on the chain length of the alkane solvent: with shorter alkanes, the alkene selectivity decreases. However, the effect of alkane chain length decreases with decreasing alkene size. These chain length selectivity effects can be explained by a pore filling mechanism, in which smaller molecules (cfr. hexene) can pack more easily in the same space as large ones (cfr. dodecene). The large set of binary adsorption isotherms determined on NaY are fitted with Langmuir based adsorption isotherm models.

Unexpectedly, the more efficient packing of small compared to large alkenes becomes more pronounced at increasing alkene loading. When studying the competitive adsorption of equimolar hexene/dodecene mixtures from an alkane solvent (heptane, decane or undecane), the separation factor of the alkenes increases with increasing alkene loading. At very low external alkene concentrations, both hexene and dodecene are adsorbed in small amounts and the cage mainly contains solvent molecules. When further increasing the external alkene concentration, the limiting amount of dodecene adsorbed remains 0.5 molecules per supercage, while hexene replaces the solvent and fills up the FAU micropores, leading to a maximum adsorption capacity of 25 alkene  $\text{CH}_x$ -groups per supercage.

The packing induced selectivity effects observed on NaY also occur on zeolites NaX and CsY, containing respectively more and bigger cations than NaY.

Molecular size induced packing effects are also observed for the adsorption of aromatics from alkanes and alkenes on NaY. While benzene, toluene and m-xylene are able to fill 84% of the supercage volume, the maximum adsorption capacity for mesitylene amounts only 64% of the supercage volume. This unexpected capacity reduction is attributed to a different pore filling mechanism. Because of steric constraints, mesitylene packs less efficiently compared to smaller aromatics, so that an additional alkane solvent molecule is still capable to co-adsorb with mesitylene in the same supercage.

In contrast to their adsorption at low coverage, aromatics are more selectively adsorbed on (i) Na-FAU compared to Cs-FAU and on (ii) Y compared to X zeolites in liquid phase conditions. The preferential adsorption of aromatics on Na-FAU compared to Cs-FAU is

explained by a more difficult packing caused by the presence of large Cs cations. The higher selectivity for aromatics on Y compared to X zeolites is caused by two different effects. The first effect applies to all aromatics and is a skewed adsorption on the SII cations because of the presence of SIII/SIII' cations. This leads to a large steric disadvantage inside the NaX supercages that are completely saturated with hydrocarbons. The second effect, which is only related to the adsorption of benzene, is an inhibited adsorption in the 12MR-window site because of the presence of cations on SIII/SIII' cation sites.

Small lab-scale breakthrough experiments using hexene/dodecene/alkane mixtures confirm the selective adsorption of short alkenes over long alkenes. Pilot-scale breakthrough experiments show that in the absence of an alkane solvent a separation factor as large as 9.2 is obtained for a 50-50 weight percentage hexene/dodecene mixture. Finally it is demonstrated that NaY is more suitable than NaX for the separation of an alkane/alkene/aromatic mixture by means of breakthrough experiments.