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Exploiting Pore or Cavity Size and Shape in Separating Linear and Branched Hydrocarbons by Inverse Selectivity: Enthalpy, Entropy and Packing Effects

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Abstract. Different enthalpic, entropic and packing effects occurring in zeolites are reviewed which can be used to control elution order in the gas and liquid phase separation of linear and branched alkanes. Ordering effects in ZSM-5 can be used to separate long linear alkanes, even when only different by one carbon. Inverse selectivity occurs with stronger adsorption of the shorter chain, and azeotropes can be formed. Preferential adsorption of branched over linear alkanes (inverse selectivity) was for the first time experimentally determined for some mono- and multi-branched isomers in MCM-22 (rotational entropy effect) and at low coverage in SAPO-5 (enthalpy effect). These selectivity reversals identified both in gas and liquid phase can potentially be useful in more efficient hydrocarbon processes such as the production of clean gasoline with high octane number.

Keywords: hydrocarbon, inverse shape selectivity, energy, entropy, molecular packing

1. Introduction

Refineries are under increasing pressure to reduce olefins, benzene, total aromatics content and try to avoid adding oxygenates to gasoline. Sufficiently high octane numbers can then only be achieved by higher contents of mono- and preferably multi-branched alkanes. This requires isomerization of the linear fraction coupled to separation of the branched components, such as with 5A zeolites. Linear hydrocarbons are able to enter the pore network and are very strongly adsorbed, and the branched compounds are eluted first. The regeneration of the adsorbent is however suffering from the slow desorption of the linear compounds, which are then returned to the isomerization reactor. There is no selectivity for the more highly branched compounds. Materials that would rather preferentially adsorb the branched compounds, or even be selective for the more highly branched ones, would potentially allow for better operation of the integrated reactor/separator unit.

Most zeolites unfortunately prefer the linear over the branched compounds and are hence not more suitable than 5A. Similarly, there could be an advantage in having materials that would preferentially adsorb shorter over longer linear hydrocarbons, as again most materials would normally more strongly adsorb the longer alkanes.

In this paper, three mechanisms for inverting the above mentioned selectivities are experimentally investigated and demonstrated to offer a potential for use in improved separations or reactor/separator systems. Data in both liquid and gas phase are given to support the proposed mechanisms: enthalpy or entropy driven separations and packing effects.

Chromatographic experiments at low coverage were performed to study the adsorption properties of these zeolitic adsorbents (Ruthven, 1984). Linearity of the experiments and absence of diffusion limitations was confirmed with different amounts of injection and

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using different carrier flow rates. Detailed explanation of the experimental setup and procedure can be found elsewhere (Ocakoglu et al., 2003).

From the temperature dependence of the Henry coefficients, the adsorption enthalpy is calculated according to:

$$K' = K_0' e^{\frac{-\Delta H_0}{RT}} \tag{1}$$

The adsorption entropy was calculated using (Schenk et al., 2003):

$$\Delta G_0 = -RT \ln(K' \rho_c RT) \tag{2}$$

and

$$\Delta S_0 = \frac{\Delta H_0 - \Delta G_0}{T} \tag{3}$$

with ρ_c the zeolite crystal density, T the temperature and R the universal gas constant. Liquid phase results were obtained by batch adsorption experiments (Denayer et al., 2003).

2. Liquid Phase Separation of Linear Alkanes in ZSM-5 Using Packing Effects

Zeolites are known for their ability to separate bulk liquid mixtures on the basis of steric or equilibrium effects. Linear hydrocarbons cannot be separated in the liquid phase by most zeolites, as these do not show the high selectivities encountered in the gas phase. However, for small pore zeolites, the tight fitting between molecules and the zeolite framework together with the high adsorption potentials results in extremely large selectivity effects in multicomponent adsorption.

The liquid phase adsorption of pure C_5-C_{22} linear alkanes on ZSM-5 was studied using a batch adsorption technique (Denayer et al., 2003). Saturation capacities of the alkanes depend strongly on the chain length (Fig. 1). The number of CH_x groups adsorbed per unit cell drops steeply between heptane and octane and then increases steadily to reach a plateau of 53-54 for C_{14}–C_{22}. In this plateau region, the pores of ZSM-5 are densely packed with alkane molecules. The mechanisms of packing in liquid phase were studied using configurational bias grand canonical Monte Carlo simulations (De Meyer et al., 2003). These simulations revealed that the probability to bend and cross in the intersections increases with chain length, explaining the very good packing of long chain alkanes. Short alkanes tend to stay away from the intersections, resulting in a lower packing density.

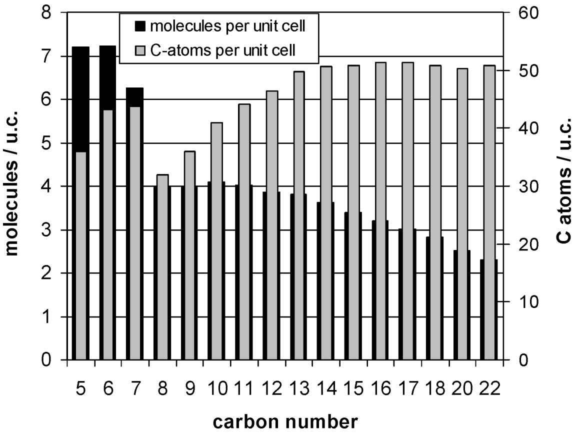


Figure 1. Pore filling in ZSM-5 by linear hydrocarbons.

A large set of adsorption isotherms of binary mixtures of long chain alkanes (up to C22) on ZSM-5 was measured to determine the effect of this alkane packing on the competition between short and long alkanes. Unexpected selectivities depending on even small differences in carbon numbers were found. In some binary alkane mixtures, adsorption of the longer chain is favored, in others the shorter chain, and azeotrope formation as well is encountered (Fig. 2). These results were analyzed in terms of pore geometry, packing efficiency and entropy effects, and again simulations were performed. Up to C12, the simulations also predicted rather well the amounts adsorbed and the resulting selectivities over the full concentration range (Chempath et al., 2004). Each time the chain length of the molecules allows for somewhat or very different packing of the molecules in the pores, deviations from the normal selectivity for the longer chain is found.

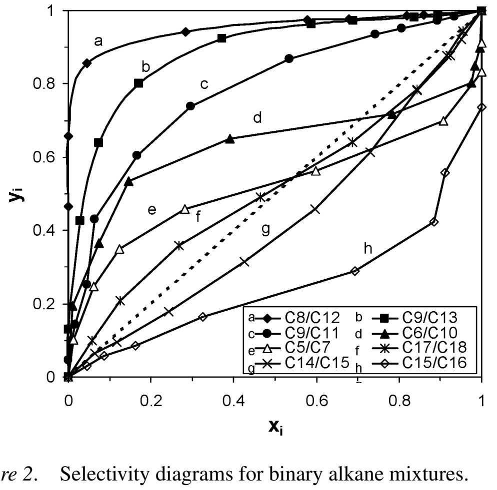


Figure 2. Selectivity diagrams for binary alkane mixtures.

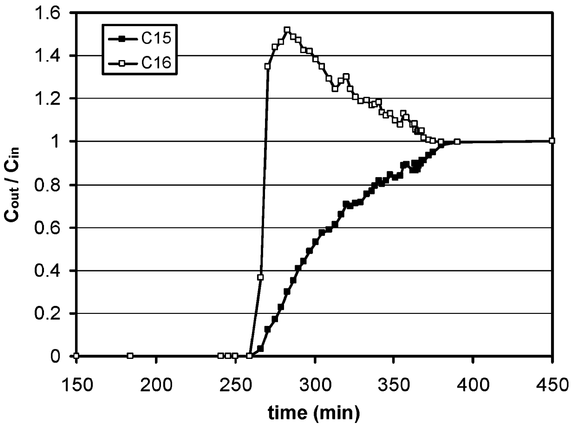


Figure 3. Breakthrough profiles of an equimolar mixture of pentadecane and hexadecane on a 12 cm ZSM-5 column.

From Fig. 2 it is seen that the C15/C16 mixture shows a spectacular selectivity reversal. To verify this feature, a breakthrough experiment with an equimolar mixture of C15/C16 was performed. Figure 3 shows the eluent to be clearly enriched with the C16 at first confirming the stronger retention of the C15 and the resulting selectivity reversal.

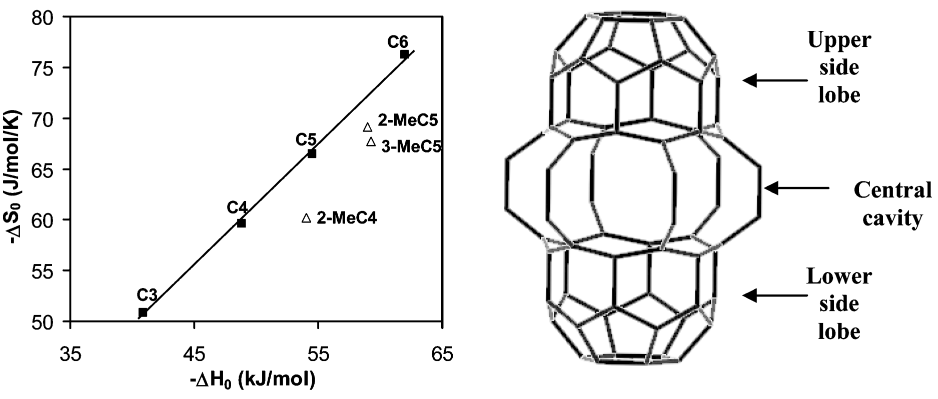
3. Selectivity Reversal for Branched C5 and C6 Alkanes on MCM-22: Entropy Effect

The adsorption of C5 and C6 isomers in MCM-22 was investigated and the results are given in the form of a compensation plot (ΔS_0 vs. ΔH_0) in Fig. 4(a). Clearly, the isomers have less energetic interaction with the zeolite walls, but are more strongly adsorbed by an entropic advantage over the linear molecules.

This is understandable if one inspects the MCM-22 cavity in Fig. 4(b) (Lawton et al., 1998), where the more compact branched isomers can be shown to freely rotate in either the side lobe or central cavity (see Fig. 2(b)) for C5 and C6 respectively, resulting in a rotational entropic advantage over the linear molecule that is too long to do so.

The result of these specific interactions in terms of separation can be seen in Fig. 5. Mordenite (Fig. 5(b)) shows the most frequently encountered normal selectivity with preference for the adsorption of the linear form, and MCM-22 rather for the branched forms (Figs. 5(a) and (c) for C5 and C6 isomers respectively). Although the preference for a more compact molecule has been predicted theoretically (see example of SAPO-5 below), this phenomenon was only found at high coverage or high pressure. Here, it is for the first time shown experimentally to occur both in the Henry low coverage region (separation factor of 1.9 at 200°C for C5 − 2MeC4) and in liquid hase adsorption, although with somewhat smaller selectivity (1.4 at room temperature).

As MCM-22 has supercages which are accessible through 10 ring apertures, these allow easy access to both linear and monobranched isomers, but size exclusion occurs for doubly branched isomers such as 2,2-dimethylbutane as in Fig. 5(c), explaining their rapid elution from the column. This material might hence be used advantageously in reaction–separation trains as used for high octane gasoline production (C5-C6 fraction).



(a)

(b)

Figure 4. Compensation plot for C3-C6 in MCM-22 (a); Structure of MCM-22 supercage with central cavity and side lobes (b).

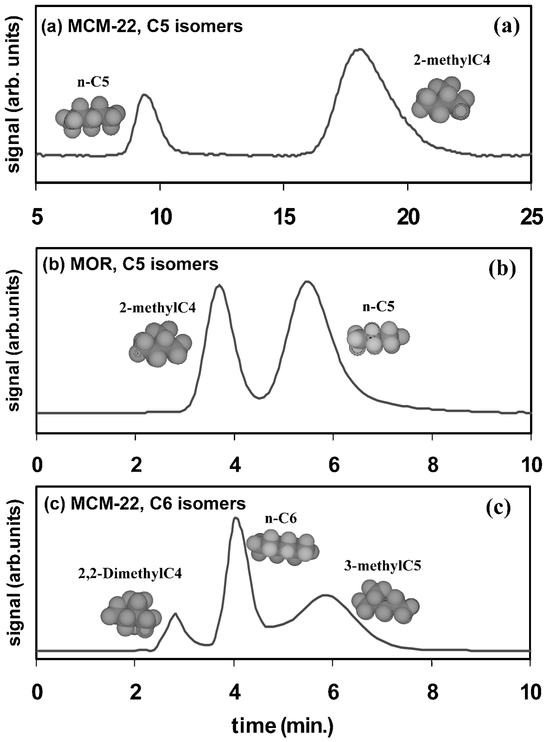


Figure 5. Normal selectivity in MOR (b), inverse selectivity in MCM-22 for C5 isomers (a) and C6 isomers (c).

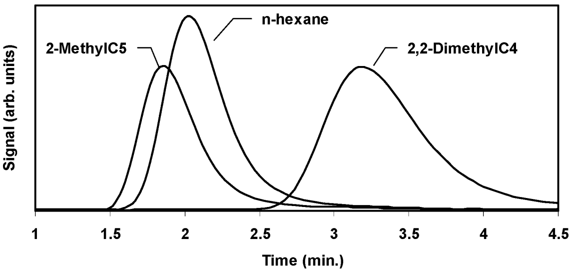


Figure 6. Gas chromatograms for normal hexane, 2-methylpentane and 2,2-dimethylbutane.

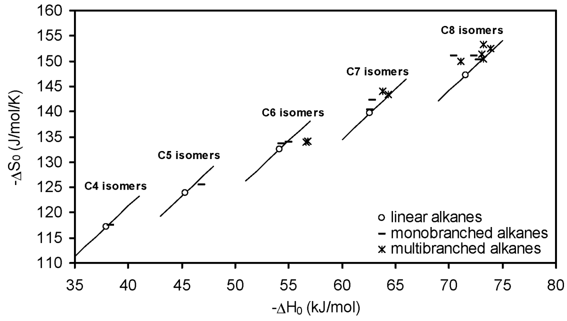


Figure 7. Compensation chart showing normal and inverse selectivities in C4 to C8 isomers.

4. Selectivity Reversal for Branched C4 and C5 Alkanes on SAPO-5: Enthalpy Effect

Santilli et al. measured a preferential uptake at high coverage of the more bulky 2,2-dimethylbutane from its mixture with 3-methylpentane and *n*-hexane on zeolites SSZ-24 and SAPO-5, both zeolites with a pore size of 7.3 Ångstrom, whilst other zeolites they tested with either smaller or larger pores were not showing this behavior. Molecular simulations (Santilli, 1993), used to calculate heats of adsorption at low zeolite coverage, indicated that in pores with a diameter between 6 and 8 Ångstrom, with a maximum at 7.3 Ångstrom, branched hexane isomers are stabilized by attractive interactions and hence adsorb more strongly. The overly simplified calculation with strong assumptions, even neglecting entropy, was later repeated (Schenk et al., 2003) and showed a small preference for 2,2 dimethylbutane over *n*-hexane, rather because of a smaller entropy loss at high loading as the branched molecule packs more efficiently in the pores, considered to be a general principle.

However, the conclusion that this can be generalized and entropy and not enthalpy is driving this type of selectivity reversal is then equally incorrect. At high coverage this might be true, but our new measurements at low coverage show the inverse selectivity only occurs with some of the C4-C6 isomers. From the compensation chart in Fig. 7, it is seen that it is due to a stronger interaction and mainly a higher adsorption enthalpy, as was proposed by Santilli. The separation factor at low loading (1.6 for 2,2-diMeC4 vs. n-C6) is much lower than at high loading measured by Santilli (4.5) and entropic packing effects, as proposed by Schenk et al., probably need to be considered to explain this higher selectivity. At low coverage, selectivity reversal occurs if the isomer point in the compensation chart falls below the line of constant Gibb's free energy (the lines in Fig. 7) through the *n*-alkane point.

5. Conclusion

The example in Fig. 8 shows the possibility to change the elution order of the C6 isomers by selection of the proper material. The thermodynamic analysis shows that for ZSM-22 (Ocakoglu, 2003), the pore mouth adsorption mechanism for the branched compounds and

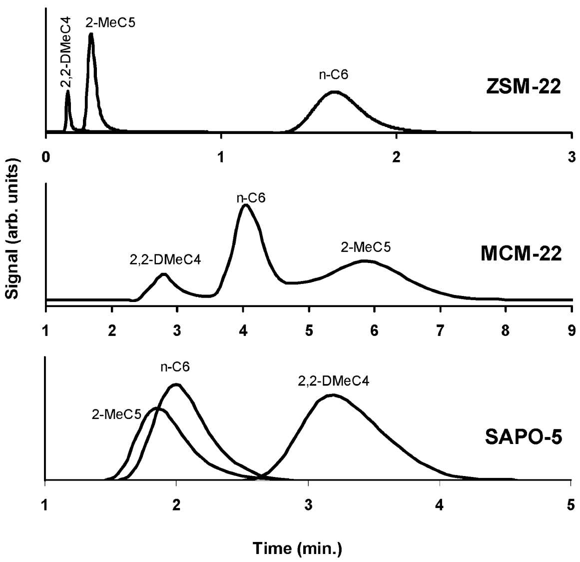


Figure 8. Controlling the order of elution of C6 isomers by adsorbent material selection ZSM-22, MCM-22 and SAPO-5.

strong adsorption of the linear molecule inside the micropores result in the "normal" selectivity, although by a very different mechanism than in say MOR. MCM-22 and SAPO-5 then give different and inverted orders of elution by respectively an entropic and enthalpic effect. Although we are in no way able to predict these results in a straightforward way, at least the present thermodynamic analysis helps in rationalizing the behaviour of the materials.

Acknowledgments

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