Selective Adsorption of Diastereoisomers in Zeolites

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3,4-Dimethylhexane is separated in part into its diastereoiosomers by selective adsorption in zeolite NaZSM-5.

Stereoisomers are usually classified into enantiomers and diastereoisomers. While the separation of enantiomers, *e.g.* by adsorption, necessarily requires a centre of chirality,[1] diastereoisomers differ, at least in principle, in all physical properties. Hence, their separation by selective adsorption can be envisaged, even if the adsorbent lacks centres of chirality. However, since the differences in the physical properties of diastereoisomers are often very small, extremely selective adsorbents are needed for such separations. Here we report on a distinct enrichment of one diastereoisomeric
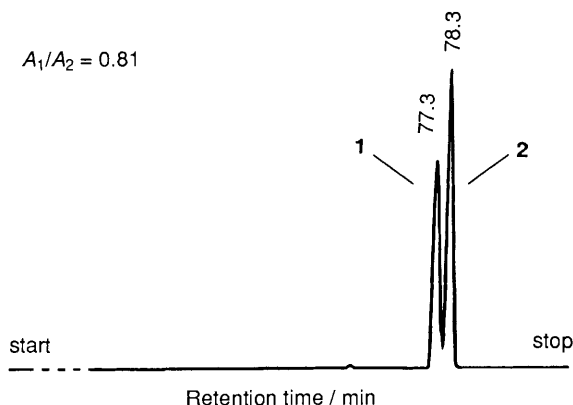
$A_1/A_2 = 0.81$

Fig. 1 Example of the gas chromatographic analysis of the 3,4-dimethylhexane diastereoisomers **1** and **2**, (A = peak area)
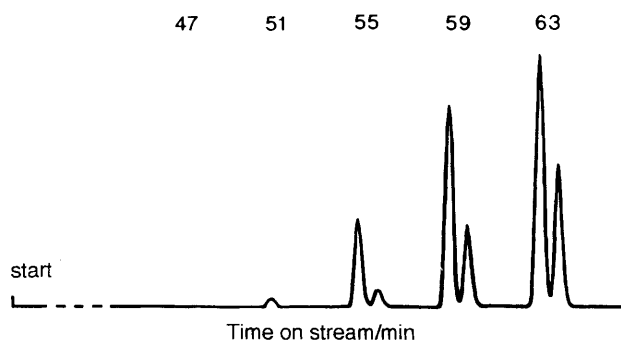

Fig. 2 Chromatograms of the adsorber effluent after different times on stream (adsorbent: NaZSM-5, n_{Si}/n_{Al} = 20, T = 120 °C)

Fig. 3 Breakthrough curves for the 3,4-dimethylhexane diastereo-isomers on zeolite NaZSM-5, (n_{Si}/n_{Al} = 20, T = 120 °C). Diastereo-isomers: ○ = **1**, □ = **2**.

form of 3,4-dimethylhexane, *i.e.* the smallest alkane which forms diastereoisomers, in zeolite ZSM-5.

The adsorption experiments were performed in a flow-type apparatus with a fixed bed adsorber at ambient pressure and temperatures up to 120 °C. The partial pressure of 3,4-dimethylhexane amounted to *ca.* 1 kPa. Typically, the mass of dry adsorbent was 0.6 g and the flow of the carrier gas (H_2) was 12 cm³ min⁻¹. A satisfactory analysis of the 3,4-dimethylhexane diastereoisomers was achieved by capillary gas chromatography under carefully optimized conditions: two columns, both with an internal diameter of 0.2 mm, were arranged in tandem. The first column (length 25 m) contained dimethyl-polysiloxane (OV-1) as the stationary phase and the second column (length 50 m) contained 5% diphenyl-/95% dimethyl-polysiloxane (SE-54). The mobile phase was hydrogen with a flow rate of 1.2 cm³ min⁻¹. The column was operated isothermally at 5 °C. A typical gas chromatogram of commercially available 3,4-dimethylhexane is presented in Fig. 1. The diastereoisomeric forms of the alkane are well resolved. In all commercial samples, the diastereoisomers were found to be present in relative concentrations of *ca.* 45:55% (A_1/A_2 = 0.81) which, presumably, corresponds to equilibrium. So far, attempts to assign the two peaks unambiguously to the diastereoisomeric forms of 3,4-dimethylhexane, *i.e.* the 3*R*, 4*S* (*meso*)-form and the 3*R*,4*R*/3*S*,4*S*-racemate, were unsuccessful. Therefore, they are denoted as diastereoisomers **1** and **2**. Breakthrough curves for both **1** and **2** were obtained by analysing the gaseous adsorber effluent at intervals which were short compared to the breakthrough times. Samples were taken by an automatically activated valve every four minutes.

In initial screening experiments, a large number of zeolites with different pore widths were tested as adsorbents. However, whereas the effective pore width of, *e.g.*, zeolite
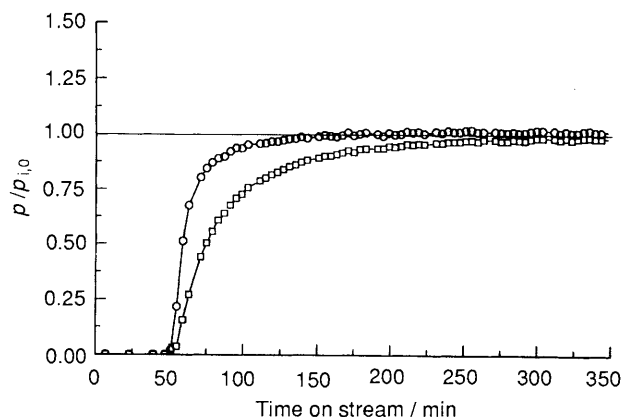
ZSM-23 proved to be too small for the envisaged separation, the pores of, *e.g.* zeolite Y were found to be much too large. In none of these and related zeolites could any enrichment of one diastereoisomer be achieved. By contrast, a clear and reproducible effect was observed on various forms of zeolite ZSM-5. Fig. 2 clearly demonstrates that for NaZSM-5 with an Si : Al-ratio of 20 and a crystallite size of *ca.* 0.5 μm, during the breakthrough phase, there is a pronounced enrichment of diastereoisomer **2** in the zeolite. After a time on stream of 51 min a trace of 3,4-dimethylhexane appears in the adsorber effluent; it consists exclusively of **1**. Somewhat later, diastereoisomer **2** appears as well, however, the ratio of the peak areas largely differs from the one in the feed. A_1/A_2 is now significantly above unity. Ultimately (not shown in Fig. 2), A_1/A_2 reaches its original value, namely when the zeolite is completely loaded with hydrocarbons.

Fig. 3 shows the complete breakthrough curves for the same experiment with NaZSM-5 as adsorbent. The enrichment of diastereoisomer **2** in the ZSM-5 adsorbent is again obvious. From the breakthrough curves, a total loading of 8.1 wt% of 3,4-dimethylhexane (based on the mass of the dry adsorbent) is calculated. The separation factor for this experiment [see eqn. (1)], amounts to 1.5 (x and y denote the mole fractions in the adsorbate phase and in the fluid feed phase, respectively). Similar enrichments of **2** were obtained on various other forms of ZSM-5, such as HZSM-5 or silicalite-1, and on zeolite ZSM-11 which, in its structure, is closely related to ZSM-5.

$$\alpha_{2/1} = \frac{x_2/x_1}{y_2/y_1} \tag{1}$$

To our knowledge, this is the first example for selective adsorption of diastereoisomers in a zeolite. The precise reasons for the ability of pentasil type zeolites to enrich one diastereoisomeric form of 3,4-dimethylhexane are not yet known. Currently, we are looking in detail at the parameters which influence the separation factor in the systems 3,4-dimethylhexane/ZSM-5 and 3,4-dimethylhexane/ZSM-11. Further work is under way in our laboratory to extend diastereoisomer separations in molecular sieve adsorbents to compound classes other than alkanes.

Reference

1 A. E. Comyns, G. W. Morris and J. P. Sankey, (Laporte Industries Ltd.), Eur. Pat. Appl., 182 170, 1986.