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Published in:
Zeolites

DOI:
10.1016/0144-2449(90)90050-2

Published: 01/01/1990

Document Version
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

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Determination of adsorption isotherms for 1-heptene adsorbed on synthetic NaX- and NaY-zeolites from n-heptane solutions

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This work presents the adsorption isotherms of 1-heptene, obtained from 10% solutions in n-heptane, on NaX and NaY zeolites. The adsorption isotherms were determined by column liquid chromatography (I.c.) by the frontal technique, followed by repetitive gas chromatographic analyses of the I.c. eluate fractions.

Keywords: NaX and NaY zeolites; adsorption, liquid phase, 1-heptene

INTRODUCTION

Synthetic molecular sieves are currently used, both in the laboratory and in industry, for the separation of various hydrocarbon mixtures. The adsorption properties of zeolites may be characterized by adsorption isotherms, which can be determined by several chromatographic techniques.1-6 For the study of adsorption systems showing hysteresis, however, only frontal analysis (f.a.)1 can be applied.

The aim of this work was to investigate the possibilities of the f.a. procedure for rapid chromatographic evaluation of synthetic zeolites, used for industrial separations of n-alkenes from reaction mixtures with n-alkanes. Several zeolites were tested by separating a model mixture (10% of 1-heptene in n-heptane) by column liquid chromatography (I.c.). Since an I.c. detector for selective and sensitive determination of the n-alkene in the n-alkane solution was not available, the I.c. experiments were evaluated by gas chromatographic analysis of the eluates.

EXPERIMENTAL

Materials

Three types of zeolites were tested:
(1) Type NaX with a ratio SiO₂:Al₂O₃ = 2.84.
(2) Type NaY with a ratio SiO₂:Al₂O₃ = 5.30.
(3) Type AgY.
All zeolites were of 0.25–0.315 mm granularity. Prior to testing, they were activated by heating 4 h at 773 K.

Column liquid chromatography (I.c.)

Glass columns (100 mm × 5.7 mm i.d.) were filled with activated zeolites. Twenty-five milliliters of the 10% solution of 1-heptene in n-heptane was fed into the chromatographic column. The adsorbed heptene was then washed out from the column by adding 10 ml of heptane with a flow 0.15 ml/min. The quantitative desorption of heptene was checked by substituting heptane by more polar desorbents (toluene and methanol). After each 0.5 ml of eluate collected, a 0.1 µl sample was taken for the determination of heptene by gas chromatography.

Gas chromatography (g.c.)

A CHROM 4 gas chromatograph (Laboratorní přístroje, Prague, Čechoslovakia) equipped with an FID was used. A glass column (3.5 m × 3 mm i.d.), packed with Chromatov N–AW coated with 15% Carbowax 6000 (both from Lachema, Brno, Czechoslovakia) was used.

RESULTS AND DISCUSSION

From the desorption curves, obtained by the f.a. method for 1-heptene desorbed from synthetic zeolites by n-heptane, the adsorbed amounts a₁ (each
Adsorption isotherms for 1-heptene on NaX- and NaY-zeolites: D. Hružík et al.

Figure 1 Desorption curve for 1-heptene in n-heptane from NaX zeolite, (x) first measurements; (O) duplicate data. $V_R =$ volume of mobile phase collected (ml); $c =$ concentration of 1-heptene in the eluate (weight percentage); $V_M =$ column hold-up volume.

Figure 2 Adsorption isotherms for 1-heptene in n-heptane on zeolites NaX (O), NaY (x), and NaY pressed to granules without granulation additives (∆), measured at 293 K. $a =$ absorbed amount (mmol/g); $c =$ see Figure 1 legend.

Figure 3 Desorption curve for 1-heptene in n-heptane from the zeolite AgY. $V_R =$ volume of mobile phase; coordinates, see Figure 1 legend.

Adsorption data for 1-heptene on NaX and NaY-zeolites: D. Hružík et al.

Adsorption isotherms (points of the adsorption isotherm) were calculated from the equation:

$$a_i = \frac{P_i}{P} \cdot Q$$

where $P_i$ is the part of the area of the desorption curve that corresponds to the concentration of 1-heptene ($c_i$), $P$ is the total area under the desorption curve (Figure 1), and $Q$ is the zeolite capacity for 1-heptene, determined by graphic integration of the area below the desorption curve (mmol of 1-heptene/g of zeolite). Experiments were carried out in duplicate for each type of zeolite. The reproducibility of the measurements was very good, yielding single desorption curves for duplicate measurements. The recovery of 1-heptene by desorption with n-heptane (at the end of the desorption curve) was determined by washing the column with toluene. The desorption of 1-heptene by n-heptane from the NaX and NaY zeolites was found to be complete. The adsorption isotherms for 1-heptene from n-heptane for the three zeolites used are presented in Figure 2. The adsorption isotherms for the NaY zeolites show steeper slopes than for the NaX zeolite. The greatest slope of the adsorption isotherm, corresponding with the highest adsorption capacity for 1-heptene, was found for the NaY zeolite not containing halloysite as a binding agent.

The adsorption properties of the AgY zeolite, prepared from the NaY zeolite by cation-exchange reaction, were also studied. Because of specific bonds, 1-heptene is very strongly adsorbed on the AgY zeolite. The desorption of 1-heptene by n-heptane from the NaY zeolite is very slow, and n-heptane displaces mainly the 1-heptene present in the dead volume of the column (Figure 3). The amount of 1-heptene ($Q_1$) eluted by n-heptane, as determined by graphic integration of the area below the curve in Figure 3, is very small ($Q_1 = 0.19$ mmol/g). The remaining 1-heptene adsorbed on the AgY zeolite surface was desorbed by sequential desorption using 10 ml of toluene and methanol each. Toluene eluted an amount $Q_2 = 0.90$ mmol/g and methanol $Q_3 = 0.72$ mmol/g of 1-heptene.

The adsorption capacities for 1-heptene of the investigated zeolites are presented in Table 1. Com-

<table>
<thead>
<tr>
<th>Type of zeolite</th>
<th>$Q$ (mmol/g)</th>
<th>$Q$ (mmol/cm$^3$)</th>
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<tbody>
<tr>
<td>NaX</td>
<td>1.50</td>
<td>0.58</td>
</tr>
<tr>
<td>NaY</td>
<td>1.39</td>
<td>0.84</td>
</tr>
<tr>
<td>NaY without binding agent</td>
<td>1.66</td>
<td>0.73</td>
</tr>
<tr>
<td>AgY</td>
<td>1.81</td>
<td>1.38</td>
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</tbody>
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Adsorption isotherms for 1-heptene on NaX- and NaY-zeolites: D. Hrůzík et al

Comparison of the data shows that Q values of the Y-type zeolites are greater than those of type X. From the comparison of the Q values (Q = 1.66 for the NaY zeolite without binding agent, and Q = 1.39 for the NaY zeolite containing 20% of halloysite as binding agent), it can be judged that the halloysite does not adsorb 1-heptene. After conversion of mass capacities into volume capacities Q, however, the results are reversed since the specific weight of the zeolite without binding agent is lower. Similarly, the higher specific weight of the AgY zeolite, as compared to the other zeolites investigated, causes nearly a twofold greater Q value for AgY than found for NaY without binding agent.

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ZEOLITES, 1990, Vol 10, March 215