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Effect of Adsorbent Preparation Parameters on the Selectivity for Xylene Isomers Separation

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Abstract

The effect of preparation parameters on selectivity of adsorbents used for *p*-xylene recovery was studied. Experiments were carried out according to a complete 2^3 design. The adequate regression equations derived for the periodic and continuous ion exchange mode showed that the latter mode gives better selectivities. The significant participation of potassium cation in the separation process was confirmed in broad parameter interval. As a further part of the study, preparation of an adsorbent form useful for industrial purposes was undertaken. A binding material was chosen and the effect of the binder on sorption capacity, separation efficiency, and mechanical resistance was determined. On the basis of these studies a lot of adsorbent was prepared and utilized in a pilot plant erected for separation of xylene isomers.

INTRODUCTION

As is well known, isomeric xylenes and ethylbenzene constitute a mixture which is difficult to separate in the simplest possible way, i.e., by distillation. As a matter of fact, ethylbenzene and *o*-xylene can be separated from other isomers but the columns employed must be of high efficiency and the reflux ratios used must be very high. However, the small difference between the normal boiling points of *m*- and *p*-xylenes, 0.753 K, makes a distillative separation of these isomers quite impractical. Therefore, resort to methods involving crystallization to separate these isomers by virtue of the large difference in their melting points, extraction, and adsorption had to be taken. However, the necessity of applying low temperatures (~ 200 K for crystallization, ~ 270 K for extraction) and corrosive media (HF-BF_3) speaks unfavorably of the former (i.e., crystallization or extractive process), and it is

the adsorptive process that is becoming increasingly superior. Both the UOP Parex and the Toray Industries Aromax processes, commercially on stream for a few years, and the recent Exxon processes have shown *p*-xylene to be obtainable by a continuous adsorptive method at a purity level at least as high as that afforded by the crystallization processes but in higher yield and at lower cost. In these processes, modified by ion exchange with barium and potassium cations, faujasite-type zeolites are used on which *p*-xylene is preferentially adsorbed (1-3). Unfortunately, because of commercial importance there is no information in the open and patent literature about the preparation parameters leading to high selectivities of adsorbents. It is a purpose of this work to show the influence of preparation variables on the adsorbent's selectivity.

EXPERIMENTAL

Polish commercial sodium faujasite with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 5.02 was used. Zeolite was kindly supplied by Chemical Works Inowroclaw. Radio-graphically, it was pure faujasite.

To describe how an adsorbent is useful for a given process, the separation coefficient has been introduced, defined as

$$B_{X/Y} = \frac{\left(\frac{X, \text{ mol-\%}}{Y, \text{ mol-\%}} \right)_{\text{ads}}}{\left(\frac{X, \text{ mol-\%}}{Y, \text{ mol-\%}} \right)_{\text{nads}}}$$

where *X* and *Y* represent the more and less sorbed components, and the subscripts "ads" and "nads" denote the adsorbed and bulk phase, respectively.

Studies on the effect of preparation variables on selectivity were performed with the aid of statistical design of experiments. To establish the design matrix the following variables were chosen:

$$\begin{aligned} x_1 &= \text{Ba/Na} \\ x_2 &= \text{K/Na} \end{aligned}$$

which are the ratios (in gram-equivalents per gram-equivalents) of cation introduced in the initial solution to the sodium content in the zeolite, and

$$x_3 = \text{temperature of ion exchange}$$

The initial parameters sets and experiment steps were

$$\begin{array}{ll} x_1^\circ = 2 & s_1 = 0.5 \\ x_{(2)}^\circ = 1.5 & s_{(2)} = 0.5 \\ x_{(3)}^\circ = 333 \text{ K} & s_{(2)} = 30 \text{ K} \end{array}$$

The response functions were selectivities for *p*-*m*-xylenes ($y_1 = B_{p/m}$) and for *p*-xylene-ethylbenzene ($y_2 = B_{p/etB}$). The ion exchange was carried out periodically (superscript *p*) or in glass columns (superscript *c*).

RESULTS

Since our previous studies (4) have shown that the best selectivities are obtained when, during ion exchange, barium and potassium cations are introduced simultaneously, so in this work these two cations were henceforth introduced in this manner.

The regression equations obtained for each operation mode were

$$\begin{aligned} y_1^p &= 6.0 - 0.24z_1 + 1.46z_2 + 0.05z_3 \\ y_2^p &= 4.31 - 0.25z_1 + 0.95z_2 + 0.02z_3 \\ y_1^c &= 6.48 - 0.68z_1 + 2.06z_2 - 0.12z_3 \\ y_2^c &= 4.33 - 0.34z_1 + 0.80z_2 - 0.22z_3 \end{aligned}$$

where

$$z_1 = \frac{x_1^\circ}{0.5} - 4$$

$$z_2 = \frac{x_{(2)}^\circ}{0.5} - 3$$

and

$$z_3 = \frac{x_{(3)}^\circ}{30} - 11.1$$

Whether periodical or column, the exchange shows the effects occurring to be identically directed, except that the column operation affords the better results (the first term in the equation is larger).

At the same time, the influence of the potassium cation on selectivity was confirmed to occur over broader parameter intervals. The regression equations also indicate that, within the range examined, temperature has the least effect on selectivity. Higher separation coefficients are obtained at low x_1

values (that is, in the region of low Ba^{2+} content). The selectivities obtained are rather high. It should be mentioned that these adsorbents contained no binding material.

Since water content in the adsorbent is not an insignificant factor for separation, further studies dealt with the effect of thermal treatment upon the adsorbent's efficiency over a broad range. The results in Table 1 show that the optimum activation temperature range varies from 573 to 773 K.

As already indicated, the adsorbent prepared contained no binding material. Once the continuous ion-exchange mode was shown to be superior to the periodical, it was deemed advisable to prepare the adsorbent in an industrially utilizable shape, i.e., to form the zeolite prior to ion exchange in a fashion as simple as possible and with the aid of readily available means. Out of a number of binders, bentonite was selected and a series of experiments was carried out to study the effect of bentonite addition on the sorptive and mechanical properties of the zeolite. The results are summarized in Table 2. The data of this table were used to select the zeolite containing 20% of the binder for further investigation. Recalculation of the sorption capacity drop in relation to the starting NaY showed the effect to be attributable (within the limits of experimental error) to the dilution of the system.

However, a binding clay added to the zeolite may also affect the selectivity of adsorbents. To determine this effect, a series of preparation experiments was performed by using the continuous ion-exchange method and by applying the initial parameter sets as in previous experiments, with due allowance for the reduced sodium content in a binder-containing zeolite weight. Thus designed, the experiments permitted elimination of the effects of all the preparation variables, except for the forming step. Results of the selectivity tests are summarized in Table 3, and for purposes of comparison, supplemented with the values obtained with binder-free adsorbents. The results indicate that the binder containing adsorbents give rise to the lower selectiv-

TABLE 1
The Effect of Thermal Treatment on Adsorbent's Selectivity

Experiment no.	Activation temperature (°K)	$B_{p/m}$	$B_{p/etB}$
1	373	1.32	1.12
2	573	3.26	2.42
3	773	3.51	2.89
4	973	2.78	2.37
5	1173	1.00	1.00

TABLE 2

The Effect of Bentonite Addition on Sorptive and Mechanical^a Properties of Adsorbents

Sample no.	Wt-% of clay addition	Sorption capacity ^b (wt-%)	Mechanical resistance ^b (wt-%)
1 ^c	5	—	—
2	10	19.3	80.9
3	15	19.0	87.0
4	20	18.6	97.8
5	25	18.0	88.1

^aAfter calcination at 923 K.

^bMean of two measurements less than 0.5% apart.

^cPowder.

TABLE 3

Comparison of Selectivities of Adsorbents Prepared from a Formed and Nonformed Zeolite

Selectivities for zeolites ^a			
Formed		Nonformed	
$B_{p/m}$	$B_{p/etB}$	$B_{p/m}$	$B_{p/etB}$
7.20	4.75	10.41	5.90
6.60	4.30	7.85	4.54
4.76	3.08	5.08	3.97
3.40	2.20	4.49	4.16
7.25	4.96	10.61	5.87

^a $\frac{K + \frac{1}{2}Ba}{Na}$ (in gram-equivalents). This was identical for formed and nonformed zeolites.

ities. It should also be emphasized that the dilution of the system with another solid which is indifferent toward C_8 isomers is of no consequence to the selectivity coefficient determinations because, for calculating the selectivity, the ratio of the quantities of individual isomers is taken in the adsorbed and bulk phases. In other words, if bentonite were a neutral component, viz., a diluent, the resulting selectivity coefficient should be identical in either case. Since this is not the case, the effect of bentonite may be explained in two ways. One explanation is to assume that bentonite exhibits some separation ability toward the mixture of xylenes, different from that inherent in the BaKNaY zeolite. The resulting lower selectivity would thus be explained by the net effect of the two adsorbents involved, the zeolite and the

bentonite. The separation properties of bentonite can be established easily by measuring the selectivity coefficients.

Another explanation is to eliminate the separation ability of bentonite and to seek recourse to the effect of new bentonite-zeolite bonds on the selectivity.

The selectivity coefficients determined for bentonite were $B_{p/m} = 1.08$ and $B_{p/etB} = 0.98$, thus showing bentonite to have practically no separation ability toward the C_8 isomers, whereby the observed drop of selectivity in the adsorbents formed prior to ion exchange must have been due to the formation of new bonds which otherwise are evident as the peaks appearing in thermograms at 870–900 K.

Based on these above-mentioned studies we prepared a tentative 50 kg lot of the adsorbent and used it in a pilot plant for continuous separation of C_8 isomers. The purity of *p*-xylene obtained was 99.3–99.4 wt-%, which shows the adsorbant to be useful in the continuous adsorptive process with simulation of a moving bed.

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