

SORPTION SELECTIVITY OF NaY-AND KY-ZEOLITES FOR XYLENE AND TOLUENE

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Abstract — The selective adsorption capacities of NaY- and KY-zeolites for xylene isomers and toluene were investigated by measuring the rate of unidirectional diffusion in a batch adsorber and the breakthrough behavior in a fixed-bed column. The sequence of sorption selectivity was found as m-xylene > toluene > p-xylene with NaY-zeolites and as the converse with KY-zeolites. The reversal of selectivity could not be explained by the molecular sieving effects but by the interactions between adsorbing molecules and cation as well as among adsorbing molecules themselves.

INTRODUCTION

The mixture of C₈ aromatics can be separated by selective adsorption on zeolites and a large number of patents have been published on this topic. Notably in 1970's U.O.P. has developed the PAREX and SORBEX processes which separate C₈ aromatics using faujasite-type zeolite. The effects of different molecular size on diffusion rate were studied by Moore and Katzer [1] and Satterfield and Cheng [2,3]. Breakthrough curves of xylene isomers in fixed bed using Y zeolite were obtained by Santacesaria, et al. [4]. The majority of the published literature is oriented to find the zeolites showing the better separation capability or to interpret the breakthrough curves through numerical simulations. However, little has been known on the separation mechanism or the qualitative interpretation of diffusion rate. A knowledge on the diffusion rate and selectivity is essential to the interpretation of the breakthrough curves in fixed bed separation processes where two or three species compete for the adsorption site.

The objective of the present paper is to analyze the separation mechanism of xylene isomers on NaY and KY zeolites. The selectivity of p-xylene over m-xylene is reversed in NaY- and KY-zeolites. This interesting phenomenon is to be analyzed in terms of the interactions between the cation and the xylene molecule as well as among the adsorbing molecules. The traditional explanation by the effect of molecular diameter does not seem to serve the purpose.

EXPERIMENTAL SECTION

(1) Sample treatment:

The NaY- zeolites were obtained from Strem Chemical Inc. in 1/16" pellet form. The KY- zeolites were prepared by ion exchange with 1 M KCl solution (initial pH=5.7) at a boiling point. Complete replacement of Na⁺ with K⁺ was assumed after repeating the ion exchange three times, each of which took about 20 hours. After the completion of exchange the KY- zeolites were washed with distilled water until AgCl was not precipitated. The samples were ground and the sizes between 30 and 50 mesh were taken for the experiment. The samples were loaded in a 5 ml glass bottle and before each measurement water was removed by heating them for 5 hours at 10⁻² torr and 400°C.

(2) Unidirectional diffusion:

Multicomponent liquid mixtures, consisting of 1 ml of each of toluene, m-, and p-xylene and 20 ml of isooctane, were kept at 50°C in a constant thermal bath. About 4 grams of NaY- or KY-zeolites were poured into the liquid mixture. At each interval of planned time, about 0.01 ml were sampled for gas chromatographic analyses. The permeation of isooctane into zeolite powders is considered negligible due to the rapidity of toluene diffusion. The diffusion measurements were carried out with and without mixing by a magnetic stirring bar to check the effect of external mass transfer resistance in the liquid phase.

(3) Fixed-bed performance:

The breakthrough curves at 50°C were obtained by

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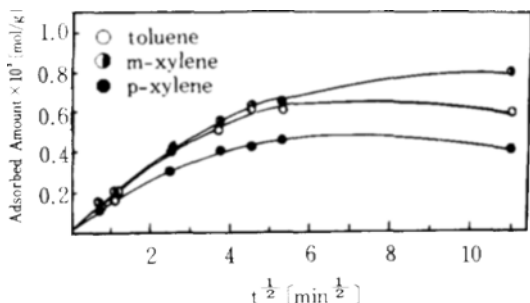


Fig. 1. Adsorption capacity of NaY-zeolites without mixing at 50°C.

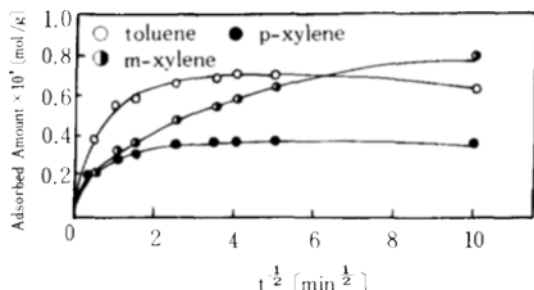


Fig. 2. Adsorption capacity of NaY-zeolites with mixing at 50°C.

analyzing the outlet streams from the fixed-bed with a diameter of 5.7 mm and a length of 30 cm, which was loaded with about 4 grams of preheated zeolites. The fixed-bed was initially filled with a solution of 16.6 volume percent toluene in isooctane. The inlet stream was a mixture of m- and p-xylene with 8.3 volume percent each in a isooctane solution and introduced as a step change: In one case, o-xylene was included in the inlet stream. The flow rate of feed stream is fixed at 0.24–0.26 ml/min, and there was no appreciable pressure drops over the zeolite bed.

RESULTS AND DISCUSSIONS

(1) Unidirectional diffusion:

With NaY-zeolites, the steady state selectivity was established after about 100 minutes. As shown in Fig. 1 and 2, m-xylene has the highest steady state selectivity. The sequence of selectivity is

$$\text{m-xylene} > \text{toluene} > \text{p-xylene}$$

At the beginning of adsorption, however, the order of selectivity is greatly influenced by the solution mixing. The transient behavior of m-xylene remains nearly the same, but those for toluene and p-xylene show very quick saturation due to the mixing and even higher selectivities than m-xylene. This indirectly indicates that

with NaY-zeolites m-xylene has higher adsorption strength than p-xylene or toluene.

With KY-zeolites, the sequence of selectivity is the opposite to that with NaY-zeolites as shown in Fig. 3 and 4. The steady state selectivity has the order as

$$\text{p-xylene} > \text{toluene} > \text{m-xylene}$$

The mixing gave much bigger influence on the saturation rate with KY-zeolites. The steady state was achieved more rapidly, only after 5 minutes with stirring the solution. As can be seen in Fig. 4, m-xylene was adsorbed instantaneously and replaced by p-xylene.

The difference or the selectivity reversal between NaY- and KY-zeolites should be analyzed in terms of the parameters affecting the adsorption selectivity. The parameters are (1) the sieving effect due to the pore and molecular sizes, (2) the interaction between adsorbing molecules and cation, and (3) the interaction among adsorbing molecules. Only with the sieving effects, p-xylene or toluene would not only have a better selectivity than m-xylene but also show a faster saturation. Moreover the sequence of performance should be the same with both NaY- and KY-zeolites. One may speculate that KY-zeolites gave the expected selectivity, but the instantaneous saturation by m-xylene rejects this notion. It was also reported by Moore and Katzer⁽¹⁾ that the adsorption of m-xylene on NaY-zeolites can not be explained by the effect of molecular size.

As for the interaction between cation and adsorbing molecule, the Na⁺ ion has a bigger polarizing power than the K⁺ ion. Therefore it is expected that more polar m-xylene has a better selectivity with NaY-zeolites. On the other hand with the KY-zeolites, the larger molecular diameter of K⁺ ion increases the chances of intermolecular interactions among adsorbing molecules within the crystalline supercage. If the interactions among molecules are large, the repulsion force can be

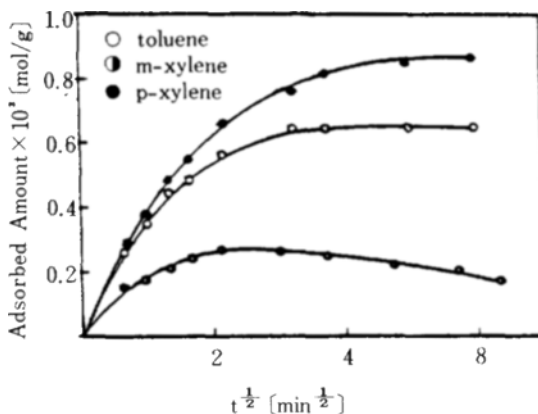


Fig. 3. Adsorption capacity of KY-zeolites without mixing at 50°C.

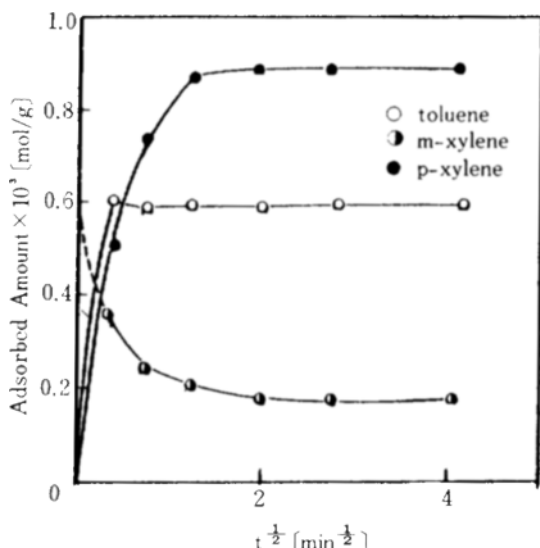


Fig. 4. Adsorption capacity of KY-zeolites with mixing at 50°C.

high enough to hinder the adsorption capability. It is presumed that the intermolecular repulsion force is predominant inside the crystalline cage of KY zeolites. Furthermore with more polar molecules, the intermolecular interaction can be considered higher and m-xylene shows a lower selectivity.

According to Ruthven and Derrah [5], the zeolitic diffusion coefficient can be expressed based on the activated process,

$$D_2 = D_0 \exp[-(E_w - \Delta H)/RT]$$

The activation energy is due to the effect of the cage window, E_w , and also due to the heat of adsorption, ΔH . Since the sieving effect is negligible for the present system, the adsorbing strength is a controlling parameter. Recently a calorimetric analysis by San-

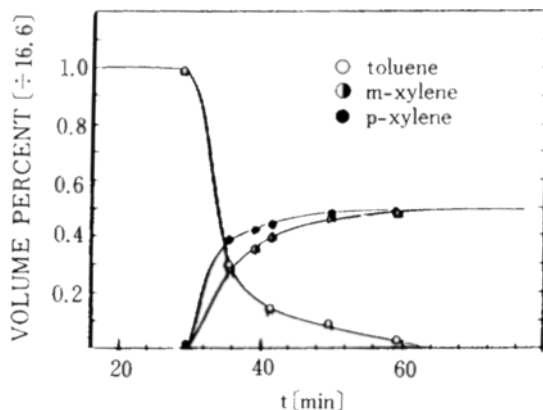


Fig. 5. Breakthrough curves for m- and p-xylene mixture over NaY-zeolite.

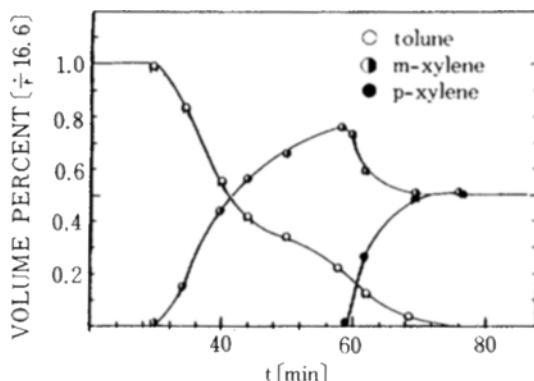


Fig. 6. Breakthrough curves for m- and p-xylene mixture over KY-zeolite.

tacesaria et al. [6] provides the data on the heats of adsorption. At 150°C, m- and p-xylene have the enthalpy changes of 30 and 27 Kcal/mole with NaY-zeolites, and 17 and 25 Kcal/mole with KY-zeolites. The reversal of selectivity with NaY- and KY-zeolites was explained by the abrupt change in enthalpy of m-xylene. It is now proposed again in the present work that this abrupt change is due to the interactions not only between adsorbing molecule and cation but also among the adsorbing molecules.

(2) Breakthrough curves:

The separation capacity by a fixed-bed was analyzed by obtaining the breakthrough curves. Fig. 5 shows that the NaY-zeolites do not yield a good separation between m- and p-xylenes. On the other hand the KY-zeolites result in an excellent separation as shown in Fig. 6. If o-xylene is added in the feed stream, it behaves almost like m-xylene as in Fig. 7. The results through the breakthrough curves are nothing but a confirmation of the expected ones from the argument on the unidirectional diffusion. The separation process (especially the adsorption column) should be designed by considering both the steady state selectivity and also the saturation rate.

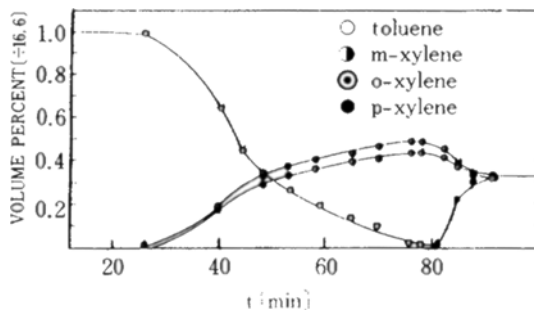


Fig. 7. Breakthrough curves for o-, m-, and p-xylene mixture over KY-zeolite.

It is noted that the molecules with higher selectivity (m-xylene for NaY-zeolite and p-xylene for KY-zeolite) are less sensitive to the external mixing as seen in Fig. 1 to 4. This seems due to the higher heat of adsorption as discussed earlier. The lower value of heat of adsorption with KY-zeolites than with NaY-zeolites suggests that the external mass transfer effect should also be taken into account for the separation with KY-zeolites.

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