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Xylene Adsorption in Liquid Phase Using a Barium-Potassium Exchanged Faujasite Zeolite

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Abstract

The separation of *p*-xylene from the other xylenes is generally made by an adsorption process, using a faujasite-type zeolite as the adsorbent. In this work, a barium and potassium exchanged faujasite was prepared (from NaY) and used to determine the adsorption isotherms of xylenes and toluene in the liquid phase. Single component and binary experiments were performed in a fixed bed column at 453, 483, and 513 K. The feed solution was diluted in *i*-octane (80-99 wt%). The isotherm curves seemed to indicate that this zeolite has higher affinity to *p*-xylene compared to the other components. The binary experiments confirmed that *p*-xylene has indeed higher affinity to the solid phase given that all breakthrough curves present roll-ups, which is evidence of the competition between these compounds during the adsorption reaction. These results will then be used to develop a Simulated Moving-Bed Reactor (SMBR) unit that will allow to maximize the isomers conversion and the selectivity towards *p*-xylene.

Keywords: xylenes; adsorption; zeolites; SMBR.

1. Introduction

Xylenes are a group of aromatic compounds widely used in the chemical industry, as its isomers, ortho (*o*), meta (*m*), and para (*p*), are used as intermediates of various compounds. *o*-Xylene is oxidized to form phthalic anhydride, while *m*-xylene is used to produce isophthalic acid, which is used in the production of unsaturated polyester resins. *p*-Xylene is the most used isomer as it can be oxidized to form terephthalic acid, which is of great relevance since it is used in the synthesis of polymers, such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) [1-3].

The separation of xylene isomers is considered one of the seven world-changing separations. The complexity of this separation is related to their similar physicochemical properties, which prevents their separation by conventional methods, such as distillation [2, 4, 5].

The separation of *p*-xylene from its isomers (and ethylbenzene) by an adsorption process employs the principles of the Simulated Moving-Bed (SMB) technology, which explores the different affinities between *p*-xylene and the other components towards the adsorbent [6]. The selective adsorption depends on the physical properties of the zeolites, such as the framework, the nature of the compensation cation, the silica-alumina ratio, and the water content [7]. Besides, the effectiveness of separation is highly dependent on the temperature.

The adsorbent normally used for the separation of *p*-xylene from its isomers in an SMB unit is a faujasite-type zeolite, X or Y, exchanged with alkali and/or alkaline earth metal ions, being preferable to use barium, potassium, or a combination of both [7-12].

This family of zeolites shows an adsorption selectivity for different isomers depending on the compensation cation, e.g., sodium is selective to *m*-xylene, while barium and potassium are selective to *p*-xylene. The selectivity to *p*-xylene also depends on the aluminum content, increasing with the silica-alumina ratio in the range of 2.4 - 6 [7].

The presence of water molecules influences both the adsorption capacity and selectivity. Water molecules interact strongly with the cations present in the framework, weakening the interactions between the aromatic ring and the cations. Therefore, in the faujasite-type zeolite, hydration levels should be around 3 - 4 wt%. For low levels of water, the selectivity of *p*-xylene over the other components decreases. On the other hand, higher water content leads to a decrease in capacity by steric hindrance because the extra water occupies the selective pore volume of the adsorbent [13]. These water molecules are not replaced during the coadsorption of xylenes because they are strongly adsorbed, favoring the adsorption of the smallest isomers, which is *p*-xylene. The affinity between the adsorbate and the adsorbent is related to entropic effects [8, 13]. At higher temperatures, the interaction between water molecules and the zeolite may cause structural modifications, which may contribute to the collapse of the structure [14]. Therefore, the adsorbent cannot be regenerated, causing its deactivation, which consequently requires its substitution [15]. Both water and xylene molecules are adsorbed near the cations which neutralize the negative charges of the framework [16].

2. Experimental

The adsorbent (zeolite Y - $SiO_2/Al_2O_3 = 5.1$) was first subjected to an ion exchange step to replace the sodium (Na^+) cations, initially present in the zeolite, with potassium (K^+) and barium (Ba^{2+}) cations through contact with a solution containing 1.0 M of barium chloride and 0.3 M of potassium chloride. The zeolite (20 g) was treated 8 times for 20 min each and then washed intensively with deionized water to remove any traces of chloride anions. This treatment took place at around 353 K, under reflux, with magnetic stirring at a speed high enough to maintain a homogenous mixture, 500 rpm in this case. The temperature was controlled by the condenser using water from the thermostatic bath.

Afterwards, the zeolite was dried overnight at 353 K. Then the adsorbent was shaped into pellets through an extrusion-spheronization process using Caleva Multi Lab-CML (Caleva, UK). The zeolite was mixed with kaolin, which acts as a binder (40 wt%). The mixing process was conducted at 80 rpm for 30 min while adding 0.42 mL of ultrapure water per gram of solid. The extrusion and spheronization processes were carried out at 60 and 650 rpm, respectively. Finally, the pellets were calcined at 823 K for 5 h.

The pellets were packed into a fixed bed column and left to dry overnight under a constant flow rate of nitrogen at 473 K. To obtain the breakthrough curves, the column was heated up to the desired operating temperature (453, 483, or 513 K) while feeding a continuous stream of *i*-octane. When the defined temperature was reached, the feed was changed from *i*-octane to a mixture of *i*-octane and xylenes (1-15 wt%) or *i*-octane and toluene (1-15 wt%). The results of these breakthrough curves were used to determine the respective isotherms. In addition, binary breakthrough experiments were also performed. In this case, the feed was a mixture of mX/pX, oX/pX, or oX/mX (5-20 wt%) in *i*-octane (80-95 wt%).

3. Results and Discussion

The adsorption equilibrium data for *o*-xylene, *m*-xylene, *p*-xylene, and toluene, obtained from the breakthrough curves, were adjusted to fit the dual-site Langmuir model. These results are represented in Fig. 1. For example, for the experiments with 1 wt% in *i*-octane at 453 K, the adsorption amounts of *o*-xylene, *m*-xylene, *p*-xylene, and toluene were 0.14, 0.17, 0.23, and 0.11 $mol \cdot kg^{-1}$ respectively.

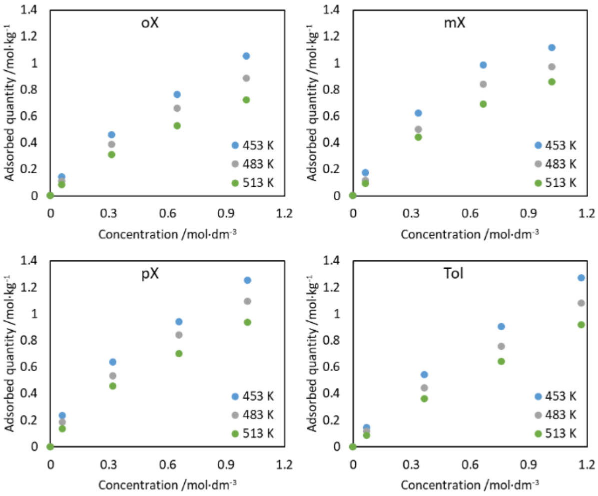

Fig. 1. Adsorption isotherms of *o*-xylene, *m*-xylene, *p*-xylene, and toluene at 453, 483, and 513 K.

The results of the binary experiments are represented in Fig. 2, one breakthrough curve for each mixture.

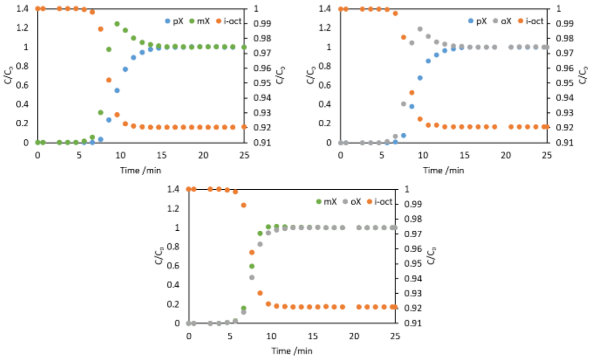

Fig. 2. Binary breakthrough curves of *o*-xylene, *m*-xylene, and *p*-xylene (10 wt%) at 453 K.

According to these results, it is possible to conclude that *p*-xylene has greater affinity towards the adsorbent than the other components, which means that it can be more easily separated from a mixture of xylene isomers and toluene. As all these components are present during the isomerization of xylenes, given that toluene is a secondary product, it could be advantageous to combine these two reactions into one single process, namely in a Simulated Moving Bed Reactor (SMBR), because by removing *p*-xylene from the reaction medium, the conversion of the other isomers can surpass the limit imposed by the thermodynamic equilibrium.

4. Conclusions

The faujasite zeolite (KBaY) shows greater affinity for *p*-xylene than *o*-xylene, *m*-xylene, and toluene, which demonstrates it is an appropriate absorbent for this separation. These are encouraging results that indicate that these reactions could occur simultaneously with isomerization (such as in a SMBR) as all these components are present.

5. Future Perspectives

The main objective of this work is to develop a Simulated Moving Bed Reactor (SMBR) process to produce *p*-xylene, employing a hybrid particle composed of both the adsorbent and the catalyst that will be used in a sorption-enhanced reactive process to maximize the isomers conversion and the selectivity towards *p*-xylene. The revolutionary aspect of this approach is the proximity between the adsorbent and the catalyst, which creates a lower resistance to mass transfer. Besides, as the separation of *p*-xylene by adsorption makes its concentration in the liquid medium decrease, isomerization of *o*-xylene and *m*-xylene can go beyond the thermodynamic equilibrium, further increasing the production of this isomer.

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