

# Xylene Separation on Plate-Like SAPO-5 Zeolite Molecular Sieves

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**Abstract**—Plate-like AFI zeolite molecular sieves (SAPO-5) were synthesized and utilized for the fixed-bed separation of industrially important feedstock of xylenes isomers. The SAPO-5 crystal powders, which were synthesized using microwave heating technique together with seeds, present homogeneous porous structure (~0.73nm), particle size, as well as low aspect ratio. Adsorption experiments indicated that the sample present strong selectivity for *o*-xylene. Fixed bed separation of different xylene mixtures were measured experimentally and modeled using the Thomas model. It was found that the model can fit the kinetics of pure xylene and binary xylene mixtures reasonably well.

**Index Terms**—SAPO-5, ZSM, fixed bed, breakthrough kinetics, adsorption

## I. INTRODUCTION

Zeolite Molecular Sieves (ZMSs) are important adsorbents in industrial separation process, because their inert surface chemistry and homogeneous porous structure which can present very high capacity/selectivity towards certain molecules [1].

The AFI framework type ZMS has one-dimensional 12-membered ring channels in the *c*-direction of the crystal [2]. Its pore size is around 0.73nm (Fig. 1a) which is among the molecular size of industrially important species such as xylenes (Fig. 1b).

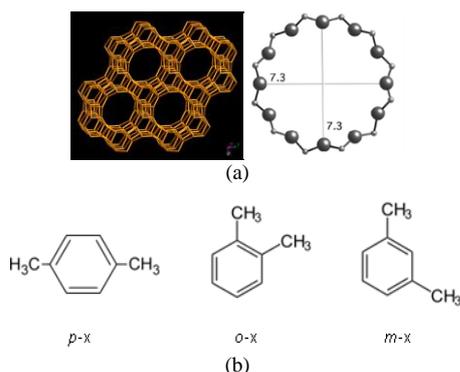


Figure 1. The structure of (a) SAPO-5 (a) and (b) xylenes

There are two isomorphs of AFI, including AIPO-5 (or AIPO<sub>4</sub>-5) and its derivative SAPO-5. The equilibrium adsorption [3] and Grand Canonical Monte Carlo (GCMC) [4] simulation showed that AIPO-5 presents a high *ortho*-selectivity of xylene isomers [5]. The adsorption capacities of xylenes on plate-like SAPO-5 crystals are slightly lower than that on AIPO-5 at 303K, but with an improved selectivity [5]. This *ortho*-selectivity is quite important in xylene separation. Current industrial processes for xylene separations are mostly based on *meta*-selectivity (NaY) or *para*-selectivity (KY, ZSM-5 and silicalite) [4]. There is no industrial process based on *ortho*-selectivity up-to-date. Thus, studying the preferential adsorption of *o*-xylene (*o*-x) over *m*-xylene (*m*-x) and *p*-xylene (*p*-x) on nanoporous SAPO-5 ZMS is of great practical importance.

The fixed-bed separation process is popularly used in chemical industries because it can handle large quantities of feed under continuous operation. The design of a fixed-bed process requires detailed system parameters and modelling/simulation works [6, 7]. However, up to now, fixed bed adsorption/separation of xylene isomers with AFI ZMS is rarely reported, except one trial run by separation of xylene mixture (*o*-x: *p*-x=1: 1 by volume) at 373K [5]. Therefore, in this research, we report the synthesis of the ZSM and the fixed bed kinetics of single component and binary gas mixture of xylene isomers on plate-like SAPO-5 crystals. The breakthrough curves will be measured under various operation conditions and mathematically modeled.

## II. SIMULATION MODEL

### A. Thomas Model for Fixed Bed Kinetics

The macroscopic mass conservation equation for a fixed bed is:

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial z} + \frac{1 - \varepsilon}{\varepsilon} \frac{\partial \bar{q}}{\partial t} - D_L \frac{\partial^2 c}{\partial z^2} = 0, \quad (1a)$$

where *z* represents the axis along the length of the fixed bed column, *t* is the time, *c* is the concentration of adsorbate in fluid phase,  $\varepsilon$  is the voidage of the fixed bed,

$v$  is the interstitial velocity,  $\bar{q}$  is the average adsorbed-phase concentration and  $D_L$  is the dispersion coefficient.

The initial and boundary conditions are

$$\begin{aligned} t = 0 &\rightarrow c = \bar{q} = 0 \\ z = 0 &\rightarrow c = \frac{D_L}{v} \frac{\partial c}{\partial z} + c_F \\ z = L &\rightarrow \frac{\partial c}{\partial z} = 0 \end{aligned} \quad (1b)$$

where  $L$  is the bed length and  $c_F$  is the concentration of the feed.

The  $\partial \bar{q} / \partial t$  term in Eq. (1) describes the adsorption rate. Thomas model [8], which assumes the Langmuir kinetics and plug flow, was adopted to model the fixed bed adsorption kinetics of each pure component of xylene isomers. The expression for the Thomas model is:

$$\frac{\partial \bar{q}}{\partial t} = k_1 \left[ c(q_m - \bar{q}) - \frac{1}{b} \bar{q} \right] \quad (2)$$

where  $q_m$  and  $b$  are Langmuir isotherm parameters and  $k_1$  is the rate constant. Ignoring axial dispersive effects, the analytical solution (pure component) derived by Thomas is

$$\frac{c}{c_F} = \frac{J(n/r, nT)}{J\left(\frac{n}{r}, nT\right) + \left[1 - J\left(\frac{n}{r}, nT\right)\right] \exp[(n - nT) \left(1 - \frac{1}{r}\right)]}$$

where

$$\begin{aligned} r &= 1 + bc_F, \\ n &= \frac{1 - \varepsilon k_1 q_m L}{\varepsilon v}, \\ T &= \frac{\varepsilon}{1 - \varepsilon} \frac{1/b + c_F}{q_m} \left( \frac{vt}{L} - 1 \right) \text{ and} \\ J(x, y) &= 1 - \int_0^x \exp(-y - \tau) I_0(2\sqrt{\tau y}) d\tau \end{aligned} \quad (3)$$

where  $I_0$  is the zero-order modified Bessel function. For multicomponent system, numerical solution of Eq. (1)-Eq. (2) has to be used. The model equations were discretized into ODEs and simultaneously solved using the finite difference method in MATLAB program.

### III. EXPERIMENTAL

#### A. Materials & Synthesis

Para-xylene (p-x), meta-xylene (m-x) (99% Reagent) and ortho-xylene (o-x) (Reagent) were supplied by Sigma-Aldrich. Plate-like SAPO-5 seeds were synthesized by microwave heating from a precursor solution with a molar composition of 1 Al<sub>2</sub>O<sub>3</sub>: 0.8 P<sub>2</sub>O<sub>5</sub>: 1 SiO<sub>2</sub>: 3.5 TEA: 50 H<sub>2</sub>O. The detailed procedure was described in reference [9] and is briefed as below: A MARS-5 (CEM) microwave oven was used as power source and a Omni control vessel (volume: 100ml, Teflon-lined) as the reactor. The reactor was fixed on a rotating turntable and under the microwave frequency of 2450MHz. The heating time ranged from 20 to 120 mins

for various precursor solutions. After the microwave synthesis, the autoclave was cooled to room temperature. The resulting solid product was washed, centrifuged, and dried at 120 °C. The SEM image and XRD pattern of the synthesized sample in Fig. 2 confirmed that the regular porous structure and morphology of the SAPO-5 sample.

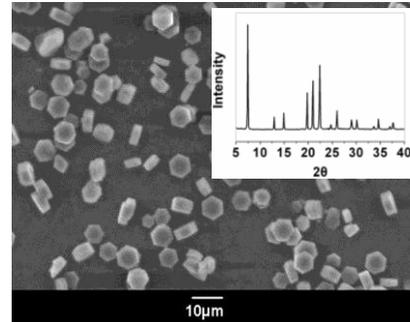


Figure 2. SEM image of SAPO-5 crystals and the XRD pattern

#### B. Measuring Xylene Isotherms

The isotherms of xylene isomers were measured on a volumetric rig at 323K and 373K. Prior to the sorption measurement, all the samples were degassed at 200 °C for 24h under high vacuum (<0.01Pa).

#### C. Measuring Breakthrough Curves

Breakthrough curves of xylene(s) were measured on a fixed bed rig shown schematically in Fig. 3. The rig mainly consists of three sections: (1) vapor/feed generator, (2) fixed bed, and (3) analytical instrument. The inlet and outlet pipelines were wrapped with heating belts to prevent possible condensation of xylene vapors.

The working principles of the fixed bed rig are described as below:

In section (1), liquid adsorbate(s) were fed to the vapor generator where it is vaporized and mixed with the carrier gas (N<sub>2</sub>). The flow rates of the liquid and gas feeds are accurately controlled by HPLC pump and mass flow controller, respectively. In section (2), the fixed bed was packed with zeolite sample powders, the temperature of which was kept constant by an oven. In section (3), the outlet concentration of the fixed bed effluents was monitored by a GC (Agilent, 7890A) with FID detector. The effluent was automatically sampled by a valve injector. The GC column was DB-WAX (Agilent) with 30m in length, 0.25mm in inner diameter (ID) and 0.25µm in thickness.

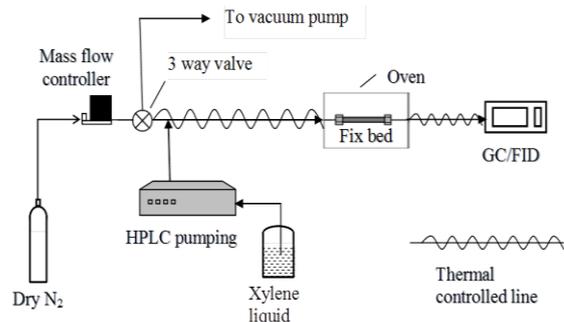


Figure 3. Schematic diagram of the fixed bed breakthrough/adsorption rig

Before the column was packed, SAPO-5 sample was cleaned/calcined at 560 °C for 12h under air atmosphere. Then 0.651g sample was loaded into the stainless steel tubing with the ID of 4.5mm and length of 60mm. Glass wool was used to hold the powdered samples in place of the fixed bed. After the packing, the fixed bed was connected to the apparatus and was purged with N<sub>2</sub> flow at 150 °C overnight, before it was brought to the experimental temperature. The breakthrough curve was measured at the designated temperature by continuously feeding a known composition of xylene vapor(s) into a stream of N<sub>2</sub> (SOXAL, Singapore). After each run, the fixed bed was regenerated by purging pure N<sub>2</sub> at 150 °C and then subject to desorption under high vacuum overnight.

#### IV. RESULTS AND DISCUSSION

##### A. Adsorption Isotherms of Xylene Isomers

The adsorption isotherm of xylene isomers were measured at a range of temperature 303-373K, and are selectively shown in Fig. 4a, and Fig. 4b, respectively. The adsorption isotherms in both figures follow the same behavior as the one obtained at 303K [5].

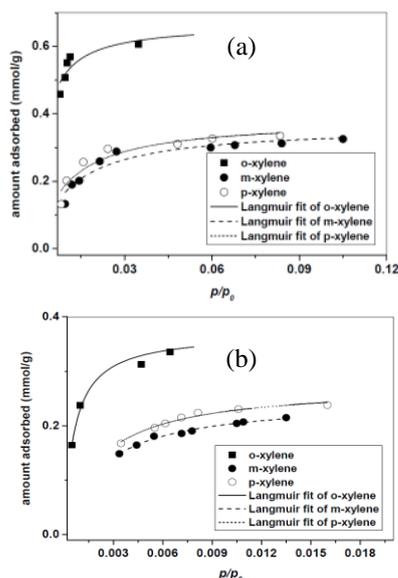


Figure 4. The isotherms of xylene isomers on SAPO-5 crystals at (a) 323K, and (b) 373K

The Langmuir equation fitted parameters for each xylene isomer under investigated temperatures are listed in Table I, where  $C_{\mu s}$  is the adsorption saturation capacity and  $b$  is the affinity. It can be seen from the table that  $p$ -x and  $m$ -x have similar adsorption properties under all the investigated temperatures. The adsorption capacities of  $o$ -x are always higher than  $p$ -x and  $m$ -x. To roughly estimate the adsorption energy of each isomer on SAPO-5, the Arrhenius plot was applied to the adsorption of each isomer at different temperature, that is:

$$b = b_0 \exp\left(\frac{E}{RT}\right)$$

where  $b_0$  is the adsorption affinity at infinite temperature and  $E$  is the adsorption energy. The adsorption energies were derived and listed in the last row of Table I. It can be seen that,  $o$ -x present a high energy of ~26kJ/mol, which is considerably higher than its counterparts. The values of these adsorption energy are a bit lower compared with their adsorption energy on AIPO-5 ZMS [10], which is 74, 64 and 54kJ/mol for  $o$ -x,  $p$ -x and  $m$ -x, respectively. Apart from the structural difference between SAPO-5 and AIPO-5, the other reason for this disparity is that the literature values were derived from the Henry's law constants obtained at very low vapor pressure. However, the adsorption energies on SAPO-5 follows the same sequence of  $E_{o-x} > E_{p-x} > E_{m-x}$  as that on AIPO-5, further confirming the *ortho*-selectivity of the SAPO-5.

TABLE I. LANGMUIR EQUATION PARAMETERS OF XYLENE ISOMERS

Temperature (K)		303 [5]	323	373	Adsorption Heat (kJ/mol)
$o$ -x	$C_{\mu s}$ (mmol g <sup>-1</sup> )	0.782	0.669	0.371	
	$b$ (KPa <sup>-1</sup> )	538.454	106.519	62.231	26.3
$p$ -x	$C_{\mu s}$ (mmol g <sup>-1</sup> )	0.516	0.385	0.275	
	$b$ (KPa <sup>-1</sup> )	109.055	22.679	14.557	26.3
$m$ -x	$C_{\mu s}$ (mmol g <sup>-1</sup> )	0.520	0.364	0.249	
	$b$ (KPa <sup>-1</sup> )	52.775	21.141	14.178	16.3

##### B. Breakthrough Curves of Single Component Xylene

Fig. 5a, Fig. 5b and Fig. 5c show the experimental breakthrough data (symbols) and the optimally fitted curves (lines) of the model for  $p$ -x,  $m$ -x and  $o$ -x, respectively. The operating conditions and the fitting parameters for each run are summarized in Table II. In general, it is seen that the Thomas model fits the experimental data reasonably well at various operation conditions, indicating the model assumptions parallel or approximate those of the underlining adsorption mechanisms at the experimental conditions (e.g. square isotherm, plug flow, homogeneous surface, Langmuir kinetics, etc.).

From the Fig. 5a-Fig. 5c and the fitting results in Table I, it can be generalized that: 1) for each component, the breakthrough time, which is defined as  $C/C_0=0.05$ , decreases as the temperature increases or the flow rate increases. The breakthrough curves become more steep (or become more vertical) when flow velocity increases, indicating a shorter mass transfer zone (MTZ) at higher flow velocity; 2) for different components,  $m$ -x and  $p$ -x present approximately similar breakthrough behaviors while  $o$ -x possesses a breakthrough time ~3 times longer.

This kinetic selectivity is in agreement with their equilibrium (isotherm capacity and affinity) properties listed in Table I.

For  $o$ -x, as the temperature decreased from 373K to 323K, its breakthrough time is more than doubled, which

corresponds to a much higher processing capability of the fixed bed and implies that the adsorption/separation may be improved at relatively lower operation temperature. At most of the operation conditions, the rate constant of *o*-x is lower than (or about half of) those of *p*-x and *m*-x at the similar operation conditions, this may be explained by its higher adsorption capacity and higher value of heat of adsorption, which hindered the mass transfer process.

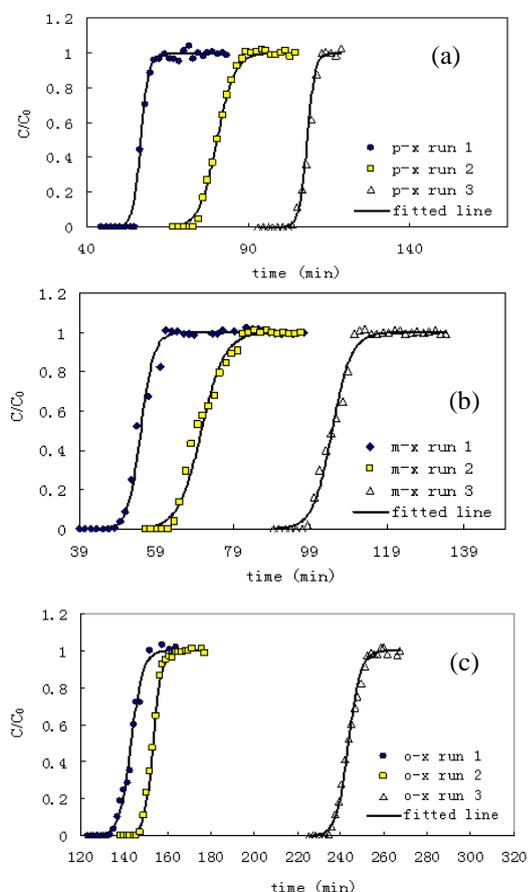


Figure 5. Experimental breakthrough curves of (a) *p*-x, (b) *m*-x, and (c) *o*-x and the simulation results (lines).

TABLE II. OPERATING CONDITIONS AND FITTING PARAMETERS OF XYLENE ISOMERS

Run no.	Temp. (K)	N <sub>2</sub> flow rate (mL/min)	Flow rate of Xylene isomer (μmol/min)	Partial pressure	Thomas rate constant $k_1$ (m <sup>3</sup> /mol.s)
<i>o</i> -x run 1	373	15	1.825	0.00298	0.013
<i>o</i> -x run 2	373	10	1.903	0.00465	0.009
<i>o</i> -x run 3	323	10	2.273	0.00556	0.004
<i>p</i> -x run 1	373	15	2.927	0.00477	0.025
<i>p</i> -x run 2	373	10	2.249	0.00550	0.009
<i>p</i> -x run 3	323	10	2.626	0.00642	0.008
<i>m</i> -x run 1	373	15	2.280	0.00372	0.03
<i>m</i> -x run 2	373	10	2.122	0.00519	0.009
<i>m</i> -x run 3	323	10	2.471	0.00604	0.008

### C. Separation of Binary Mixture

For the fixed bed separation of a binary xylene gas mixture, the component breakthroughs earlier are called the first component while the later one is called the second component. The roll-up (or overshoot) of a component is frequently seen if the system consists of a fast moving/lightly adsorbed species and a slowly moving/strongly adsorbed species. The degree of this overshoot depends on the relative strength in the diffusivity and adsorption affinity between the two components [11].

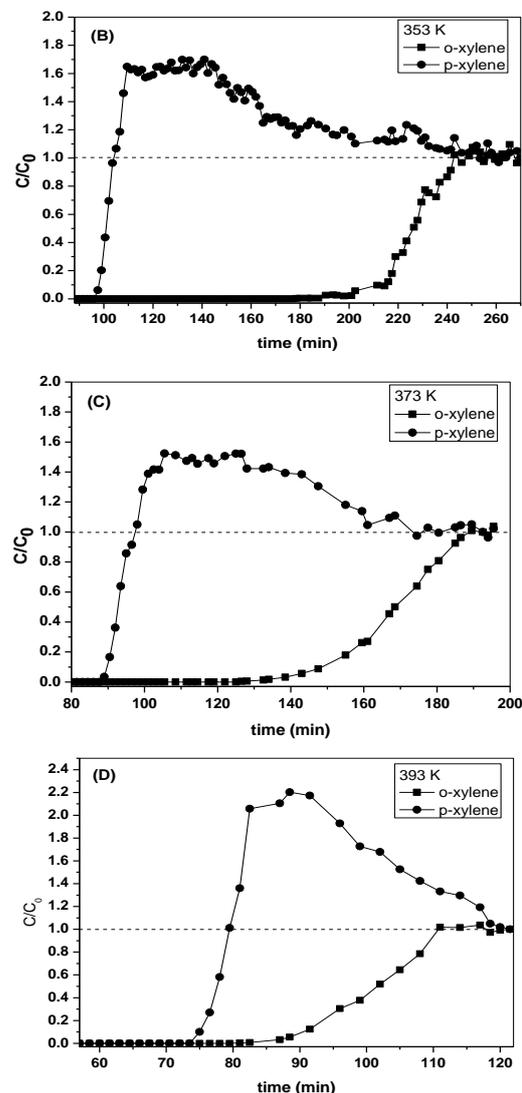


Figure 6. Breakthrough curves of *p*-x/*o*-x mixture at (a) 323K; (b) 353K; (c) 373K and (d) 393K. The Legends (a)-(d) correspond to runs 1-4 in Table III.

The fixed bed separation experiments of binary mixture of xylene vapor were conducted at different temperatures and feed compositions. The results are plotted as the normalized concentration (relative to the feed concentrations of each component) and are shown in Fig. 6 and Fig. 7 for *o*-x/*p*-x system and *o*-x/*m*-x system, respectively. It is seen that, in all cases, *o*-x is the slowly moving but strongly adsorbed species which is capable of displacing *p*-x and *m*-x from the porous network of

SAPO-5. This is in agreement with the experimental results of adsorption equilibrium and fixed bed kinetics of the pure component xylene. The difference in breakthrough time and the overshoot of p-x and m-x is a good indication of the equilibrium as well as the kinetic selectivity of the SAPO-5 towards the xylene isomers [5].

In Fig. 6, it can be seen that, as temperature increases, the overshoot degree increases marginally while the breakthrough time reduces significantly. There is also a trend that the breakthrough time will become closer to each other when temperature increases from 323K to 393K. Therefore, lower operation temperature favors the selectivity of the fixed bed separation. Similar trends were also observed for ox/m-x system (Fig. 7). These observations may suggest the adsorption equilibrium plays a more important role in the overall *ortho*-selectivity of SAPO-5 observed in fixed bed separation.

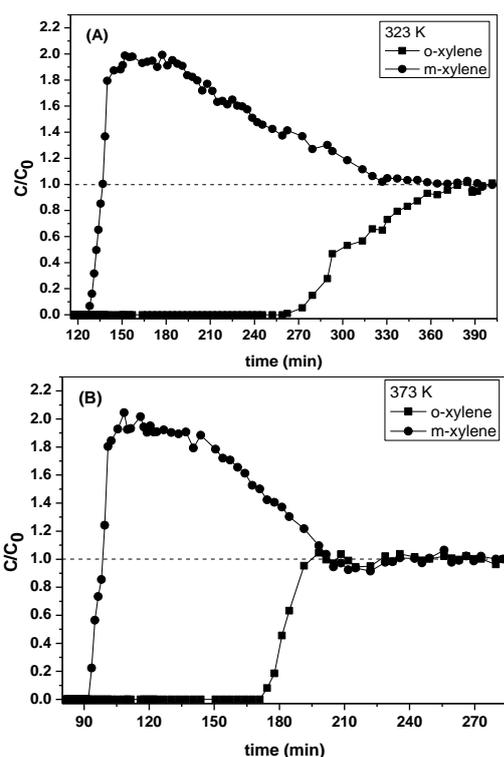


Figure 7. Breakthrough curves of *m-x/o-x* mixture at (a) 323K and (b) 373K. Legends (a) and (b) correspond to runs 5 and 6 in Table III.

TABLE III. OPERATING CONDITIONS OF FIXED BED ADSORPTION OF BINARY XYLENE MIXTURE

Run no.	Temp. (K)	N <sub>2</sub> flow rate (mL/min)	Flow rate of xylene (μmol/min)		Flow rate of xylene (μmol/min)	
			p-x	o-x	m-x	o-x
1	393	14	1.176	0.885	-	-
2	373	14	1.519	1.144	-	-
3	353	14	1.547	1.164	-	-
4	323	14	1.923	1.449	-	-
5	373	14	-	-	1.251	0.988
6	323	14	-	-	1.480	1.169

## V. CONCLUSIONS

Plate-like SAPO-5 ZSM was successfully synthesized and utilized for the separation of xylene mixtures. It was found that *o*-xylene exhibits higher adsorption capacity and affinity over its isomers under the investigated temperatures. The adsorption energy as well as the fixed bed kinetics confirmed the *ortho*-selectivity of the plate-like SAPO-5 molecular sieve in the separation of xylene. The fixed bed breakthrough curves of pure component xylene were well fitted by Thomas model. The fixed bed separation of xylene mixture was favored by lower operation temperature.

## REFERENCES

- [1] Y. Takeuchi, H. Iwamoto, N. Miyata, S. Asano, and M. Harada, "Adsorption of 1-butanol and p-xylene vapor and their mixtures with high silica zeolites," *Separations Technology*, vol. 5, pp. 23-34, 1995.
- [2] C. Baerlocher, W. M. Meier, and D. H. Olson, *Atlas of Zeolite Framework Types*. Amsterdam: Elsevier, 2001.
- [3] A. S. T. Chiang, C. K. Lee, and Z. H. Chang, "Adsorption and diffusion of aromatics in AIPO4-5," *Zeolites*, vol. 11, pp. 380-386, 1991.
- [4] S. M. P. Lucena, J. A. F. R. Pereira, and C. L. Cavalcante Jr, "Structural analysis and adsorption sites of xylenes in AIPO4-5 and AIPO4-11 using molecular simulation," *Microp. Mesop. Mater.*, vol. 88, pp. 135-144, 2006.
- [5] E. Hu, Z. Lai, and K. Wang, "Adsorption Properties of the SAPO-5 Molecular Sieve," *Journal of Chemical & Engineering Data*, vol. 55, pp. 3286-3289, Sep. 2010.
- [6] J. M. Chern and Y. W. Chien, "Adsorption isotherms of benzoic acid onto activated carbon and breakthrough curves in fixed-bed columns," *Ind. Eng. Chem. Res.*, vol. 40, pp. 3775-3780, 2001.
- [7] V. J. Inglezakis and H. Grigoropoulou, "Effects of operating conditions on the removal of heavy metals by zeolite in fixed bed reactors," *J. Hazard. Mater.*, vol. 112, pp. 37-43, 2004.
- [8] H. C. Thomas, "Heterogeneous ion exchange in a flowing system," *Journal of the American Chemical Society*, vol. 66, pp. 1664-1666, 1944.
- [9] E. Hu, Y. L. W. Huang, Q. Yan, D. Liu, and Z. Lai, "Synthesis of highly c-oriented AFI membranes by epitaxial growth," *Microporous and Mesoporous Materials*, vol. 126, pp. 81-86, 2009.
- [10] A. S. T. Chiang, C.-K. Lee, and Z.-H. Chang, "Adsorption and diffusion of aromatics in AIPO4-5," *Zeolites*, vol. 11, pp. 380-386, 1991.
- [11] K. Wang, C. Li, H. San, and D. D. Do, "The importance of finite adsorption kinetics in the sorption of hydrocarbon gases onto a nutshell-derived activated carbon," *Chemical Engineering Science*, vol. 62, pp. 6836-6842, 2007.

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