

Materials Science

Separation of Xylene Isomers in the Anion-Pillared Square Grid Material SIFSIX-1-Cu

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Abstract: Xylene isomer separation is considered one of the seven separation challenges that changed the world. In addition, the high-energy demand of xylene separation highlights the need for efficient novel adsorbents. Herein, the liquid-phase separation potential of the anion-pillared hybrid material SIFSIX-1-Cu was studied for preferential adsorption of *o*-xylene and *m*-xylene over *p*-xylene, which was inspired by a previous complexation crystallization method for separating *m*-xylene. We report detailed experimental liquid-phase adsorption experiments, yielding selectivities of 3.0 for *o*-xylene versus *p*-xylene and 2.6 for *m*-xylene versus *p*-xylene. Our theoretical calculations thus provide a reasonable explanation that the xylene adsorption selectivity is attributed to the C–H...F interaction, and the host–guest interaction order agrees with the adsorption priority: *o*-xylene > *m*-xylene > *p*-xylene.

The separation and purification of petrochemical feedstocks is essential in the laboratory and even industry and accounts for 10–15% of global energy use.^[1] In particular, xylene isomers, including *para*-xylene (*p*-xylene), *meta*-xylene (*m*-xylene), and *ortho*-xylene (*o*-xylene), are known as important raw materials. One isomer, *p*-xylene, is most desirable for producing polymers such as polyethylene terephthalate (PET) and polyester.^[2] Because they have similar sizes and boiling points, the xylene isomers are challenging to separate by conventional distillation methods except *o*-xylene (144.4 °C). Therefore, the separation of *p*-xylene (138.3 °C)/*m*-xylene (139.1 °C) is one of the barriers to obtaining xylene isomers. Current industrial separation of *p*-xylene and *m*-xylene primarily relies on crystallization (40% of global *p*-xylene production) and adsorption (60% of global *p*-xylene production).^[3] Compared to crystallization, adsorption, which has higher efficiency and lower energy consumption, is

gaining broader application. At present, the majority of adsorbents for xylene separation are *para*-preferential adsorbents, whether in industrial applications or academic research. This is mainly because the molecular size of *p*-xylene is slightly smaller than those of *m*-xylene and *o*-xylene, so the pore size of the adsorbent can be controlled to make it easily adsorb *p*-xylene. In the actual industrial application process of xylene separation, the adsorbents that preferentially adsorb *o*-xylene and *m*-xylene are more conducive to obtaining high-purity *p*-xylene products and simultaneously have higher separation efficiency. It is meaningful to study materials that selectively adsorb *o*-xylene and *m*-xylene.

Metal–organic frameworks (MOFs) are the most widely studied materials for xylene adsorption and separation, and several MOFs have been identified for the separation of important couples: *p*-xylene and *m*-xylene. For example, MAF-X8,^[4] MIL-125,^[5] MIL-125-NH₂,^[6] and JUC-77^[7] have *para*-preferential selectivity. In particular, MOFs such as MIL-53,^[8] UIO-66,^[9] Co₂(dobdc),^[10] Sqi-1-Co-NCS,^[11] and [Ni(NCS)₂(ppp)₄]^[3] exhibit selectivity towards *o*-xylene and *m*-xylene. Therefore we focus on *ortho*-selective MOFs with *m*-xylene/*p*-xylene selectivity greater than 1 and provide a summary in the Supporting Information (Table S3). According to the current research progress, several MOF materials can preferentially adsorb *o*-xylene and *m*-xylene mainly due to their unique structure and organic ligand, and these MOFs can have a strong interaction with *o*-xylene/*m*-xylene. Therefore, it is very promising to develop an MOF adsorbent that preferentially adsorbs *o*-xylene and *m*-xylene.

Herein, we focus on an anion-pillared hybrid square grid material [CuSiF₆(4,4'-bpy)₂·8H₂O] (SIFSIX-1-Cu). SIFSIX-1-Cu, which was first reported in 2000,^[12,13] belongs to a broad family of SIFSIX in which two-dimensional nets of 4,4'-bipyridine and divalent copper ion nodes are pillared with SiF₆²⁻ anions to construct three-dimensional coordination networks. To date, these novel MOFs have been widely investigated because of their structural diversity and microporous nature for CH₄ adsorption,^[12] CO₂ adsorption^[14] and separation,^[15] acetylene/ethylene separation,^[16] propyne/propadiene separation,^[17] propane/propylene separation,^[18] and water vapor adsorption.^[19] More recently, SIFSIX-1-Cu and its isomorph ZU-61 have been proven to have unique *m*-xylene/*p*-xylene selectivity in xylene gas phase separation.^[20] SIFSIX materials can adjust the pore size by changing the organic ligand to separate adsorbate molecules of different sizes, and, on the other hand, they exhibit unique selectivity in the field of adsorption separation due to

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the SiF_6^{2-} anions. SIFSIX-1-Cu has great potential for xylene separation because of its unique feature of fluorine atoms in SiF_6^{2-} anions, which is inspired by a previous complexation crystallization method for separating *m*-xylene.^[21] In this work, we found that SIFSIX-1-Cu can preferentially adsorb *o*-xylene and *m*-xylene over *p*-xylene in the liquid phase. The adsorption priority order of the three isomers is *o*-xylene > *m*-xylene > *p*-xylene. In this regard, a detailed study was carried out on this material, including structural characterizations, static single-component or binary adsorption experiments, and binary breakthrough experiment. By combining the experimental adsorption results, the adsorption mechanism was further discussed through theoretical calculations.

SIFSIX-1-Cu was successfully synthesized according to the literature,^[13] and the relevant structural characterizations are shown in the Supporting Information. The single-component adsorption isotherms were subsequently collected at 25 °C to evaluate the xylene separation behavior. It can be seen from Figure 1a that *o*-xylene was adsorbed most, followed by *m*-xylene and then *p*-xylene, and the isomers reached adsorption saturation at an equilibrium concentration near 5 wt%. Furthermore, the equilibrated adsorption uptakes of *o*-xylene increased significantly with the initial concentration. The saturation adsorption capacity of *o*-xylene reached 130.3 mg g^{-1} . The adsorption capacities of *m*-xylene and *p*-xylene were found to be 111.8 mg g^{-1} and 78.7 mg g^{-1} , respectively. The different adsorption models were used to fit the single-component batch adsorption isotherm curve (Table S1).

Competitive binary adsorption experiments of *p*-xylene versus *m*-xylene, *p*-xylene versus *o*-xylene and *m*-xylene versus *o*-xylene in batch mode also confirmed the above adsorption preference: *o*-xylene > *m*-xylene > *p*-xylene. The binary adsorption curve and selectivity calculation results are shown in Figure 1 b–d. It can be seen intuitively from the Figure that the selectivity of *m*-xylene/*p*-xylene is 2 and the selectivity of *o*-xylene/*p*-xylene is almost 3. The *o*-xylene versus *m*-xylene competitive isotherm is given in Figure 1 d, and the selectivity of *o*-xylene versus *m*-xylene is always greater than 1. The liquid-phase ternary competitive experiment results (Table 1) reveal that SIFSIX-1-Cu exhibited a preference for *o*-xylene, with *o*-xylene/*p*-xylene and *m*-xylene/*p*-xylene selectivity values of 3.0 and 2.6, respectively. In the binary adsorption experiments, the *m*-xylene/*p*-xylene selectivity of SIFSIX-1-Cu was 2.3, which is comparable to that of other *ortho*-selective MOFs (Table S3). Furthermore, breakthrough curve presented an ideal liquid-phase separation effect on *p*-xylene and *m*-xylene in Figure S2. Initially, no xylene molecule was detected in the effluent and then the *p*-xylene eluted first, indicating that *p*-xylene molecules have low affinity towards the column. From the breakthrough curve, an obvious roll-up effect was observed, that is due to when the adsorbent reaches adsorption saturation, the more preferred *m*-xylene gets to displace the less preferred compound *p*-xylene. So the elution concentration of *p*-xylene temporarily exceeded the feed liquid. This also implies that there is a competitive adsorption between *m*-xylene and *p*-xylene, which compete for the same adsorption site (fluorine atom of SiF_6^{2-}), which will be further explained in the subse-

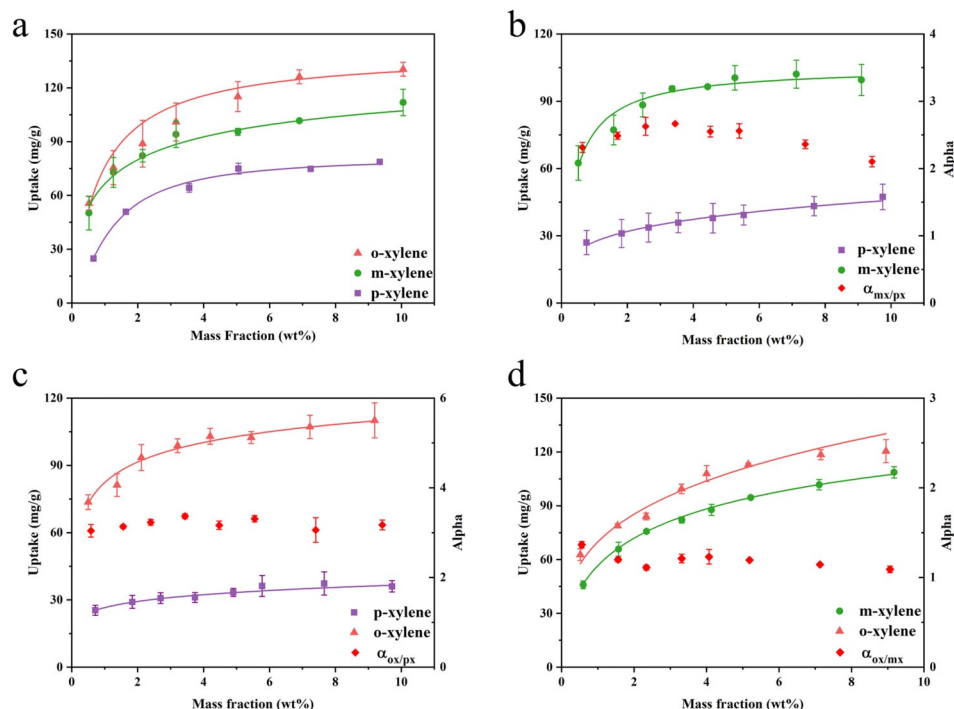


Figure 1. (a) Single-compound adsorption isotherms for *p*-xylene (squares), *m*-xylene (circles) and *o*-xylene (triangles) on SIFSIX-1-Cu at 25 °C: uptakes (mg g^{-1}) vs. equilibrium mass fraction (wt%). The binary competitive adsorption isotherms and selectivities α of *p*-xylene/*m*-xylene (b), *p*-xylene/*o*-xylene (c) and *m*-xylene/*o*-xylene (d) on SIFSIX-1-Cu at 25 °C: The uptakes (mg g^{-1}) from an equimolar mixture are shown on the left axis, which is a function of the equilibrium bulk-phase concentration of each compound. The selectivities α are given on the right axis. Error bars are all within the symbol size.

Table 1. Summary of competition experiments.^[a]

Solution	omp	om	op	mp
ox:mx:px	1:1:1	1:1:0	1:0:1	0:1:1
uptake	46.7/40.3/15.8	53.7/49.1	70.5/25.7	70.6/31.3
selectivities in liquid	3.0/2.6/1.2	1.1	2.7	2.3

[a] Uptake (mg g^{-1}) at 5 wt% equimolar binary and ternary mixtures of *p*-xylene, *m*-xylene, *o*-xylene on SIFSIX-1-Cu and selectivities $\alpha_{\text{ox/mx}}$, $\alpha_{\text{ox/px}}$ and $\alpha_{\text{mx/px}}$ are shown in the last line.

quent theoretical simulations. The breakthrough experiment with the ternary solution of equimolar xylene isomer mixture was carried out in Figure S3. The ternary breakthrough curve also proved the selectivity difference of SIFSIX-1-Cu to the three isomers. The breakthrough experiment results verified that adsorption priority was consistent with the liquid-phase batch adsorption experiments. Thus, it is worth mentioning that SIFSIX-1-Cu not only exhibits good *o*-xylene selectivity, but also offers competitive separation selectivity for the other two isomers *p*-xylene and *m*-xylene.

Molecular simulation of the interaction energies between the three xylene isomers and the SIFSIX-1-Cu square network calculated by density functional theory (DFT)^[16] (see the Supporting Information). The conformational geometries of all adsorbates and the SIFSIX-1-Cu adsorbent were optimized. As demonstrated in Figure 2, the interaction energies between *o*-xylene and SIFSIX-1-Cu were obviously lower than those between the other two isomers and SIFSIX-1-Cu, which means that the adsorption energy of *o*-xylene is stronger and that the structure after adsorbing the *o*-xylene molecule is more stable. The order of the interaction energy between xylene molecules and SIFSIX-1-Cu is *o*-xylene < *m*-xylene < *p*-xylene. *p*-Xylene has the highest interaction energy, indicating that it has the weakest interaction with the SIFSIX-1-Cu framework. In other words, the porous anion-pillared hybrid material SIFSIX-1-Cu exhibits great potential for the separation of three xylene isomers. The simulated vapor-phase adsorption isotherm of the

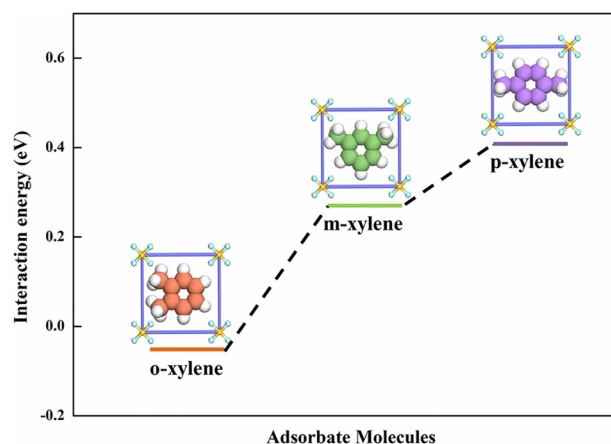


Figure 2. Interaction energies of the xylene isomers with SIFSIX-1-Cu. (a selected square grid in the SIFSIX-1-Cu framework and three isomers as illustrated. purple: *p*-xylene; green: *m*-xylene; orange: *o*-xylene).

important couple *p*-xylene/*m*-xylene also suggests that more *m*-xylene molecules can be adsorbed than *p*-xylene (Figure S1). The theoretical selectivity predicted from the isotherm simulation of an equimolar mixture is approximately 3 for *m*-xylene versus *p*-xylene, which shows little difference from the results of the batch adsorption experiment.

All the above DFT calculations and experimental results for SIFSIX-1-Cu suggest that there is a difference in the interaction between the SIFSIX-1-Cu adsorbent and adsorbate xylene molecules. To further describe the strength of this host-guest interaction, the lowest-energy configurations of the adsorbates were simulated using the sorption module with the universal force field, as illustrated schematically in Figure 3. The structural model of SIFSIX-1-Cu was built from its single-crystal data provided by Cui^[16] and then used in the adsorption simulation without further optimization. The conformational geometries of all adsorbates (*p*-xylene, *m*-xylene and *o*-xylene) were optimized before adsorption simulation. The red lines and red mark represent the probable C—H...F interaction and the distance between hydrogen atom and fluorine atom (Å). Previous literature reported that an effective separation method named solvent extraction uses the difference in basicity of xylene isomers to react with HF-BF₃ to form complexes.^[21] *m*-Xylene and *o*-xylene are more alkaline and more easily form stable complexes with HF-BF₃ to separate them from *p*-xylene. Herein, the mechanism of SIFSIX-1-Cu preferentially adsorbing *o*-xylene/*m*-xylene is probably similar. As a result, we found that compared with the distance between *p*-xylene and fluorine (2.668 Å, 4.482 Å), the distances between *m*-xylene (2.722 Å, 2.692 Å) or *o*-xylene (2.784 Å, 2.960 Å) and the fluorine atom are shorter, which indicates that the fluorine atom of SiF₆²⁻ within SIFSIX-1-Cu more easily interacts with *m*-xylene and *o*-xylene than with *p*-xylene. For *m*-xylene and *o*-xylene, the distance between them and fluorine atoms is similar, while the uptake of *o*-xylene in SIFSIX-1-Cu is higher than that of *m*-xylene in liquid-phase experiments, which may be related to their different adsorption configurations in SIFSIX-1-Cu. For the

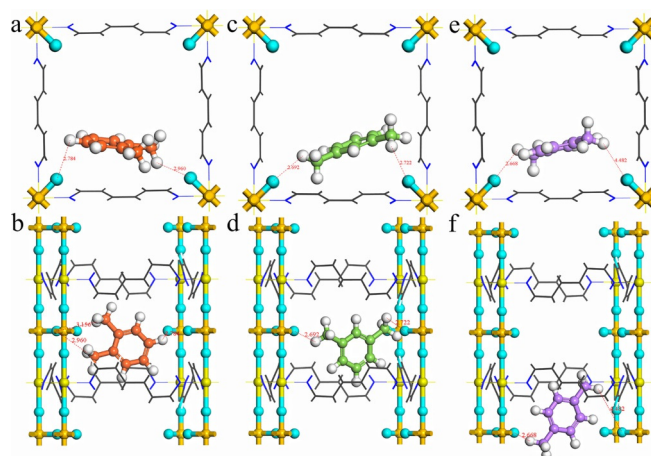


Figure 3. Simulated (a, b) *o*-xylene, (c, d) *m*-xylene and (e, f) *p*-xylene adsorptive configurations in SIFSIX-1-Cu. Color code: F, light blue; Si, yellow; C, gray; H, light gray; N, blue; Cu, brown; H (in *p*-xylene, *m*-xylene or *o*-xylene), white; C (in *p*-xylene) purple; C (in *m*-xylene) green; C (in *o*-xylene) orange.

guests in the square cavities (Figure 3a–f), *o*-xylene molecules exhibit two types of C–H...F interactions with adjacent fluorine atoms of SiF₆²⁻, including hydrogen atoms in two positions (benzene ring and methyl groups), while *m*-xylene and *p*-xylene only form the latter interaction. Therefore, the above different host-guest interactions were likely attributed to the unique molecular geometry of *o*-xylene that allows the interaction of hydrogen both on the benzene ring and on methyl groups with the fluorine atom of the frameworks, giving rise to greater *o*-xylene uptake in SIFSIX-1-Cu. On the other hand, as shown in Figure 3c, d, e and f, the position and angle of the two methyl groups of *m*-xylene make it more suitable to exist in the SIFSIX-1-Cu cages than *p*-xylene. Combined with the previous DFT-calculated interaction energies and simulated adsorption configurations, the adsorption priority of *o*-xylene > *m*-xylene > *p*-xylene was consistent with the liquid-phase adsorption experimental results.

In summary, we found SIFSIX-1-Cu not only exhibits high *o*-xylene selectivity towards *p*-xylene but also displays a considerable separation coefficient in the competitive adsorption process for the difficult separation of *m*-xylene and *p*-xylene couples. In liquid-phase adsorption experiments, the separation factors are 2.6 for *m*-xylene versus *p*-xylene and 3.0 for *o*-xylene versus *p*-xylene. DFT calculations also corroborated the experimental results and confirmed the adsorption priority order: *o*-xylene > *m*-xylene > *p*-xylene. The theoretical simulation shows that the main reason for the preferential adsorption of *o*-xylene and *m*-xylene over *p*-xylene is the strong interaction between the fluorine atoms on SIFSIX-1-Cu and the adsorbed molecules, which is due to their different molecular configurations. For the important couple *m*-xylene and *p*-xylene, preferred *m*-xylene adsorbents, including SIFSIX-1-Cu, are of great significance for the development and design of next-generation adsorbents. Given the richness of SIFSIXs with variable and tunable pore sizes and surface functionalities, it is expected that more efficient SIFSIXs will emerge for the high-efficiency separation of xylenes in the near future.

Conflict of interest

The authors declare no conflict of interest.

Keywords: anion-pillared square grid material • C–H...F interaction • host–guest systems • SIFSIX • xylene separation

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