Liquid-Phase Multicomponent Adsorption and Separation of Xylene Mixtures by Flexible MIL-53 Adsorbents

Mayank Agrawal,†‡ Souryadeep Bhattacharyya,†‡ Yi Huang,†‡ Krishna C. Jayachandrababu,†‡ Christopher R. Murdock,‡ Jason A. Bentley,§ Alejandra Rivas-Cardona,§ Machteld M. Mertens,§ Krista S. Walton,§,†‡ David S. Sholl,§,†‡ and Sankar Nair*†‡

1School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100, United States
§ExxonMobil Chemical Company, Baytown, Texas 77520, United States

ABSTRACT: The MIL-53 class of metal–organic frameworks (MOFs) has recently generated interest as potential adsorbents for xylene mixture separations. Cost-effective separation of xylene isomers is challenging owing to the similarity in their molecular structures, kinetic diameters, and boiling points. Here we report a systematic experimental and computational study of xylene isomer adsorption in MIL-53 adsorbents, focusing particularly on the effects of different metal centers, determination of separation properties with industrially relevant quaternary liquid-phase C₈ aromatic feeds, and a predictive molecular simulation methodology that accounts for all relevant modes of MIL-53 framework flexibility. Significant scale-up of MIL-53 synthesis was carried out to produce high-quality materials in sufficient quantities (300–500 g each) for detailed measurements. Single-component adsorption simulations incorporating the MIL-53 “breathing” and linker flexibility effects showed good agreement with experimental isotherms. Upon the basis of these results, three materials—MIL-53(Al), MIL-53(Cr), and MIL-53(Ga)—were selected for detailed quaternary liquid breakthrough measurements. High o-xylene quaternary selectivity was obtained from all of the MIL-53 materials, with MIL-53(Al) being the most selective. Better packing efficiency of o-xylene and its preferred interactions with the MIL-53 framework are hypothesized to lead to high selectivity. Predictions from flexible-structure multicomponent adsorption simulations showed good overall agreement with experiment. This is, to the best of our knowledge, the first experimental report on the xylene adsorption characteristics of MIL-53 materials under industrially relevant operating conditions. In addition, it is also the first attempt to develop computational methods that account for various flexibility modes in MIL-53 materials for adsorption simulations. This has significant broader applications for the successful prediction of adsorption properties of larger molecules (such as C₈ aromatic isomers) in flexible MOFs.

INTRODUCTION

The C₈ alkylaromatics are important raw materials for a variety of chemical processes.¹,² Xylene isomer product streams are obtained from processes such as toluene disproportionation, gasoline pyrolysis, or catalytic reforming of naphtha and consist of four isomers: p-xylene (pX), m-xylene (mX), o-xylene (oX), and ethylbenzene (EB).³ In purified form, all these components have commercial value as feedstocks.³,⁴ pX is widely used to produce polyethylene terephthalate (PET), which is then used in the production of polyester resins, fibers, and packaging containers. mX is used to synthesize isophthalic acid, which is used in PET resin blends. EB is dehydrogenated to styrene for polystyrene production, and oX is utilized in the synthesis of phthalic anhydride, a plasticizer. The similarity in molecular structures, close kinetic diameters (5.8–6.8 Å), and similar boiling points (138–144 °C) make cost-effective separation of these four isomers challenging, with the cost of production largely dependent on the cost of separation.²,⁴,⁵

While crystallization and azotropic distillation can be used to separate C₈ mixtures, the currently preferred separation technology is the PAREX process, which is based on simulated moving-bed adsorption.⁶,⁷ The adsorbent used is a faujasite (FAU)-type zeolite exchanged with cations like K⁺ or Ba²⁺, and it shows moderate pX selectivity attributed to xylene–cation interactions and favorable packing under high xylene loadings within the zeolite pores.⁷ Other zeolites such as MFI and ZSM-5 have also been evaluated for xylene separations.⁹–¹² Recently, metal–organic frameworks have created interest for C₈ isomer separation.¹³ Metal–organic frameworks (MOFs) are a class of crystalline nanoporous materials which have been widely studied for adsorptive separations due to their high surface area, high porosity, and structural tunability by utilizing
various combinations of metal centers and organic linkers.\textsuperscript{13–17} Among the MOFs investigated for xylene mixture separations, the MIL-47 and the MIL-53 series have shown promise for separating xylene mixtures.\textsuperscript{18–22} Both of these MOF types consist of one-dimensional (1D) pores lined with terephthalate ligands. These materials have hydroxy (MIL-53) or oxo (MIL-47) groups connected through coordination bonds to saturated trivalent (MIL-53) or tetravalent (MIL-47) metal centers.\textsuperscript{20,23} One of the most intriguing features of these MOFs is their framework flexibility, which leads to changes in crystal structure and lattice parameters as a function of temperature, humidity, and adsorption of molecules.\textsuperscript{24–29}

MIL-53 materials are especially interesting as they exhibit different framework flexibility depending on the metal center.\textsuperscript{24} Previous experimental studies have shown the potential for xylene isomer separations by MIL-53 MOFs.\textsuperscript{5,18,19,21,30,31} Finsky et al. carried out single-component adsorption and binary breakthrough experiments of C8 aromatics in MIL-53(Al) with vapor-phase feeds at 110 °C and demonstrated that framework flexibility enables selective xylene adsorption.\textsuperscript{20} Binary batch adsorption and binary breakthrough experiments in the liquid phase showed MIL-53(Al) to be oX selective.\textsuperscript{21} The binary oX/mX selectivities for dilute xylene mixtures (0.028 and 0.06 M) in hexane in this work were reported as 2.7 and 2.2, respectively, from batch adsorption and binary breakthrough measurements, respectively.\textsuperscript{21} Ternary liquid breakthrough measurements, respectively, from batch adsorption and binary breakthrough experiments in the liquid phase were reported as 2.7 and 2.2, respectively, from batch adsorption and binary breakthrough experiments in the liquid phase.

In this paper, we address the above issues systematically through a combined experimental and computational study of single-component and multicomponent C8 isomers in several MIL-53 materials. We develop computational methods to account for different types of flexibility in MIL-53 and initially validate these methods with detailed experimental single-component isotherm data from MIL-53(Al), MIL-53(Cr), MIL-53(Ga), MIL-53(Fe), and MIL-53(Sc) materials. Upon the basis of these results, we select three materials—MIL-53(Al), MIL-53(Cr), and MIL-53(Ga)—for detailed multicomponent quaternary liquid breakthrough measurements with industrially relevant xylene mixtures and operational conditions. We then compare our experimental multicomponent adsorption data with predictions from our flexible-structure multicomponent adsorption simulations, the effects of different metal centers and framework flexibility on C8 mixture separations are discussed in detail. Our experimental work also involved significant scale-up of MIL-53 materials synthesis to produce high-quality materials in sufficient quantities for the adsorption and breakthrough measurements.

\section*{EXPERIMENTAL METHODS}

\textbf{Materials.} The following chemicals were purchased from Sigma-Aldrich: 1,4-Benzene dicarboxylic acid (C6H4-C6H4-O)\textsubscript{2}, 98%, abbreviated as BDC), aluminum chloride hexahydrate (AlCl\textsubscript{3}·6H2O, 99%), chromium(III) chloride hexahydrate (CrCl\textsubscript{3}·6H2O, \geq 98%), iron(III) chloride hexahydrate (FeCl\textsubscript{3}·6H2O, 98%–102%), N,N-dimethylformamide (HCON(CH\textsubscript{3})\textsubscript{2}, \geq 99.8%, abbreviated as DMF), ethanol (C\textsubscript{2}H\textsubscript{5}OH, 200 proof, anhydrous, \geq 99.5%), hydrochloric acid (HCl, 37%), pyridine (C\textsubscript{5}H\textsubscript{5}N, 99.8%), hexane (C8H\textsubscript{18}, 99%), ox (C\textsubscript{6}H\textsubscript{5}C\textsubscript{2}H\textsubscript{5}, 99%), mX (C\textsubscript{6}H\textsubscript{4}(CH\textsubscript{3})\textsubscript{2}, 99%), EB (C\textsubscript{6}H\textsubscript{3}[CH\textsubscript{3}]\textsubscript{3}, 99.8%), EB (C\textsubscript{6}H\textsubscript{3}[CH\textsubscript{3}]\textsubscript{3}, 99.8%), pX (C\textsubscript{6}H\textsubscript{4}(CH\textsubscript{3})\textsubscript{2}, 99%), 1,3,5-trisopropyl benzene (C\textsubscript{8}H\textsubscript{16}(CH\textsubscript{3})\textsubscript{3}, 95%, abbreviated as TIPB), and toluene (C\textsubscript{8}H\textsubscript{10}, 99.5%). Hydrated gallium(III) nitrate (Ga(NO\textsubscript{3})\textsubscript{3}·xH\textsubscript{2}O, 99.9%) and hydrated scandium nitrate (Sc(NO\textsubscript{3})\textsubscript{3}·xH\textsubscript{2}O, 99.9%) were obtained from Alfa Aesar. All chemicals were used as obtained. Deionized (DI) water was obtained with an EMD Millipore water purification system.

\textbf{Synthesis of MIL-53.} MIL-53(Al), MIL-53(Cr), MIL-53(Ga), MIL-53(Fe), and MIL-53(Sc) were synthesized by hydrothermal methods as reported in the literature.\textsuperscript{27,28,34–36} However, these methods typically yielded small quantities of material (<1 g). In this work, experiments for scaling-up the MIL-53 synthesis were performed with the aim of providing high-quality materials in sufficient quantities. Approximately 500 g of MIL-53(Al), 400 g of MIL-53(Cr), and 300 g of MIL-53(Ga) were prepared. Synthesis conditions for scaled-up MIL-53 synthesis are listed in Table S1 (Supporting Information). All syntheses were performed in stainless steel autoclaves under autogenous pressure. In a typical synthesis, a stock solution was first prepared by dissolving a calculated amount of metal source with solvent(s) (1000 mL of DI water, 1000 mL of DMF, and 1000 mL of DMF + 55 mL of pyridine for MIL-53(Al/Cr/Ga), MIL-53(Fe), and MIL-53(Sc), respectively). In the preparation of MIL-53(Cr), the pH value of the stock solution was adjusted to 1.2 using HCl. Then a calculated amount (see Table S1) of the freshly prepared stock solution was added into a number of 45 mL Parr Teflon cups (maximum 26 mL in each Teflon cup). BDC (linker) was added individually in order to complete a required composition in each Teflon cup for the MIL-53 crystallization.
As an example, in a typical synthesis of MIL-53(Al), 167.5 g of AlCl₃·6H₂O was dissolved in 1000 mL of DI water to form a stock solution. Then 23.35 g of the stock solution was added to each 45 mL Parr Teflon cup, followed by further addition of 1.152 g of BDC to complete the full molar composition of 80 H₂O(3.35 g):0.5BDC(1.152 g). After mixing all of the reagents, high-power ultrasonication was applied (10–20 min) to uniformly disperse BDC in the stock solution. With the in situ dispersion method, the loss of reagents (particularly for BDC whose solubility in water is low) was minimized, as no reactor transportation was required. Loss of the linker molecules would sometimes significantly alter the initial composition, resulting in incomplete crystallization of MOFs and poor reproducibility. We observed that ultrasonication-assisted dispersion promoted the growth of highly crystallized MIL-53 with excellent reproducibility. After dispersion of BDC, the final synthesis mixtures were autoclaved and transferred to a preheated electric convection oven for the crystallization of MIL-53 samples. The product was filtered and washed with DI water (ethanol in the case of MIL-53(Sc)). As-synthesized MIL-53(Sc) was then obtained after drying in air. However, the as-synthesized MIL-53(Al), MIL-53(Cr), or MIL-53(Ga) was then purified by a solvent extraction method using hot DMF with a sample to DMF mass ratio of 1:30 at 423 K for 24–48 h to remove the unreacted BDC. Finally, the extracted samples were filtered, washed with a copious amount of DMF, and dried in air at room temperature. In the case of MIL-53(Fe), the as-synthesized samples were washed repeatedly with DI water and warm DMF and then dried in air. Finally, MIL-53(Fe)[H₂O] was obtained after dispersion into water (1 g of the solid in 0.5 L of DI water) and drying in air.

**Activation of MIL-53.** Activation of MIL-53 samples in bulk amounts (>30 g per time) was carefully examined in this work. For example, activation of as-synthesized MIL-53(Cr) and MIL-53(Ga) was typically performed by calcining a thin layer of sample (~0.5 cm thick) in a convection oven at 573 K for 24 h at the same heating and cooling rate of 1 K/min. It is worthwhile mentioning that a series of calcination temperatures were examined in this work. MIL-53(Cr) (or MIL-53(Ga)) with similar structural properties (e.g., similar BET surface area and micropore volume) can be obtained at a calcination temperature as high as 623 K when keeping the same heating and cooling rates. However, in this work, 573 K was selected as the target activation temperature for MIL-53(Cr) and MIL-53(Ga) unless otherwise stated. Fully activated MIL-53(Al) samples were obtained by heating under vacuum at 523–623 K for 24 h. MIL-53(Fe) and MIL-53(Sc) were activated at 398 and 623 K, respectively, for a period of 12 h. After soaking the as-synthesized MIL-53(Fe) in excess DI water (see Synthesis section), MIL-53(Fe)[H₂O] was obtained and can be easily activated at a much lower temperature of 398 K. The list of activation conditions can be found in Table 1 (Results and Discussion section).

**Characterization.** Activated MOF samples were characterized with powder X-ray diffraction (PXRD), nitrogen physisorption, and scanning electron microscopy (SEM). PXRD measurements were conducted on an X’Pert Pro PANalytical Xray Diffractometer in reflection Bragg–Brentano geometry operating with a Cu anode at 45 kV and 40 mA and an X’celerator detector. PXRD patterns were collected with a step size of 0.02° 2θ and scan time of 10 s/step. Nitrogen physisorption was measured at 77 K for MIL-53 samples activated at 473 K overnight using a Quadrasorb instrument. Before the measurements, MIL-53 samples were outgassed at 573 K overnight. MIL-53(Ga) samples were first outgassed at a lower temperature (473 K) for 12 h, followed by a quick heating to 593 K and further outgassing for 5 h before cooling down. The latter step was found to effectively open the pore structure of MIL-53(Ga) for physisorption measurements. BET surface areas were calculated in individually determined pressure ranges. Micropore volumes were estimated by the t-plot method. Samples were imaged on a Zeiss Ultra60 FE-SEM with a high-efficiency in-lens SE detector at a working distance of 7–8 mm and accelerating voltages of 2–5 kV. Prior to SEM observations, samples were sonicated for 10 s in methanol, dispersed on a flat Al sample holder with two-sided adhesive conductive carbon tape, and coated with gold or carbon for 30–60 s at 4.4 V using a Cressington 108A carbon coater to prevent charging effects.

**Single-Component Vapor-Phase Isotherms.** Single-component adsorption measurements were conducted using a VTi-SA vapor sorption analyzer at 323 K. Each experiment was preceded by in situ activation under a high-purity nitrogen stream at 383 K. Adsorption data were collected at adsorbate relative pressures (P/P₀) with P₀ being the saturation vapor pressure) ranging over more than 2 orders of magnitude (0.002–0.6). Each experiment included in situ activation (up to 12 h) followed by collection of approximately 15 isotherm points. At low relative pressures (P/P₀ < 0.1) each data point was collected after 6–12 h of equilibration (based on visual inspection of the real-time weight change plot). At higher P/P₀ equilibrium is typically attained in less than 3 h per point.

**Multicomponent Liquid Phase Breakthrough.** For liquid breakthrough measurements, stainless steel columns (50 mm length and 4.6 mm inner diameter) were filled with pelletized and crushed MOFs with particle sizes between 200 and 400 μm without any binder. The feed mixture was a 0.5:1:2:1 (molar) mixture of EB:Py:mXoX, and hexane was used as the desorbent. TIPB was used as a tracer. An identical column filled with inert glass beads was used to accurately determine tracer breakthrough time for calculations. Guard
columns filled with zeolites 3A and 13X were used to prevent any effects of residual moisture in the feed stream. A two-position valve was used for accurate step change and introduction of the feed mixture for breakthrough runs. The pump flow rate was set to 0.2 cc/min, and a pressure of 100 psi was maintained across the column using a backpressure regulator. The flow rate at the outlet of the column was measured with the help of a digital flowmeter (TovaTech). All runs were conducted at 323 K. The samples were collected with an autosampler with toluene as the diluent for subsequent GC analysis. A schematic of the breakthrough setup can be found in Figure S1 (Supporting Information). The adsorbed amounts q (mol/g) were first calculated for each molecule by integration of the breakthrough curves

\[
q = \frac{1}{m_{ads}} \times \int_{0}^{t} u(C_{in} - C_{out})dt
\]

Here \( u \) is the volumetric flow rate of the feed (L/min), \( C_{in} \) and \( C_{out} \) are the concentrations of the molecule at the column inlet and outlet, respectively (mol/L), \( t \) is the time (min), and \( m_{ads} \) is the loading of the MOF in the column (g). Separation factors \( \alpha_{ij} \) were calculated as

\[
\alpha_{ij} = \frac{q_i}{q_j} \times \frac{C_j}{C_i}
\]

Here \( q_i \) and \( q_j \) are the amounts of species i and j adsorbed per unit mass of MOF (mol/g) and \( C_i \) and \( C_j \) are the concentrations (mol/L) of species i and j in the external liquid phase at the column inlet. Further details of the liquid breakthrough setup are also available from our previous work.\(^{22}\)

**Stability Tests.** Both pelletized and powdered MIL-53(Al/ Cr/Ga) were investigated for their solvothermal stability in the feed mixture of EB:pX:mX:oX with a molar ratio of 0.5:1:2:1. First, 200 mg of activated MIL-53 samples (both powder and pellet) was soaked in 25 mL of the mixture and then heated to 323 K in a closed vessel under static conditions for 7, 15, and 30 days. The samples were then recovered by centrifugation at 5000 rpm for 30 min, dried in air at room temperature, and reactivated under vacuum at 573–623 K overnight. Nitrogen adsorption–desorption measurements at 77 K up to 1 bar were then performed on the samples, and the data were analyzed in the same manner as described earlier for fresh MIL-53 samples.

**Computational Methods.** Prior to adsorption calculations, MIL-53(Cr) narrow-pore and large-pore structures, initially taken from RASPA\(^{39}\) library, were geometrically optimized using density functional theory (DFT) in the Vienna ab initio Simulation Package (VASP)\(^{40,41}\) with the projector augmented wave (PAW) approach.\(^{42}\) MIL-53(Ga) and MIL-53(Al) structures were generated by replacing the metal center in MIL-53(Cr), followed by geometrical optimization using the approach detailed above. The unit cell was first fully relaxed allowing for volume changes and then relaxed with fixed cell parameters (ionic relaxation) during geometrical optimization. The cutoff energy of the plane wave basis set was 520 eV. For all simulations, the Brillouin zone was sampled with a Monkhorst–Pack grid. A k-point mesh of 2 × 3 × 5 for one unit cell of MIL-47 or MIL-53 large-pore structure and a mesh of 2 × 5 × 5 for one unit cell of MIL-53 narrow-pore structure was used. The cutoff energy and k-point mesh was tested to ensure energy convergence within 0.001 eV/atom. A conjugate gradient method was used to optimize atomic positions until the forces on each atom converged within 0.01 eV/atom. The Perdew–Burke–Ernzerhof (PBE) exchange correlation functional\(^{43}\) was adopted to perform calculations with the DFT-D2 functional\(^{44}\) to account for dispersion forces. Dispersion forces are important to capture long-range interactions such as \( \pi-\pi \) stacking in aromatic rings. Adsorption isotherms in MOFs were simulated using GCMC simulations as implemented in RASPA.\(^{39}\) Nonbonded interactions between adsorbates and the framework atoms were calculated using a Lennard–Jones (L–J) potential truncated at a spherical cutoff distance of 13 Å. Cross terms are specified using Lorentz–Berthelot mixing rules with L–J parameters taken from the DREIDING\(^{45}\) force field for the framework atoms and the TraPPE\(^{46}\) force field for adsorbates. To calculate Coulombic forces, electrostatic charges on atoms

![Figure 1](https://example.com/image1.png)
in the MOFs were assigned on the entire periodic framework using the DDEC methods.\textsuperscript{47} We used equilibration and production periods of $5 \times 10^5$ and $1 \times 10^6$ Monte Carlo (MC) cycles, respectively. In each MC cycle, adsorbate insertion/deletion, rotation, translation, and identity change moves were attempted. Coulombic interactions were computed using the Ewald method with $10^{-6}$ Ewald precision and 12 Å cutoff.

The osmotic framework adsorbed solution theory (OFAST)\textsuperscript{48,49} was used to describe structural transitions in the flexible MIL-53 frameworks. This method uses adsorption isotherms to predict the equilibrium-favored structure at given conditions. MIL-53 materials are known to exist in narrow-pore (NP) and large-pore (LP) structures,\textsuperscript{32,33,50−55} and OFAST was used to predict transitions from one structure to another. To describe swelling of the frameworks, molecular dynamics (MD) simulations were performed in the NPT ensemble at 323 K and 10\textsuperscript{5} Pa. A time step of 1.0 fs was used, and runs were carried out for 1 ns. The van der Waals interaction cutoff was set to 16 Å. The force field parameters for MIL-53 are taken from those previously reported by Ma et al.\textsuperscript{32} that used CVFF\textsuperscript{56} parameters for the organic part and UFF\textsuperscript{57} parameters for the inorganic part of the MOF. Additional simulation details of OFAST and force field parameters for MD calculations are provided in the Supporting Information (Figure S2 and Tables S2−S6). Table S7 shows the DFT-optimized lattice parameters for the MIL-53 materials.

**RESULTS AND DISCUSSION**

Figure 1a shows the PXRD patterns of the activated MIL-53 (Al/Cr/Ga/Fe) materials synthesized using our scaled-up methods. The crystal structures were all determined to be of the narrow-pore (NP) form. MIL-53 adsorbents exhibit reversible structural transformations from LP form to NP form upon adsorption of some guest molecules (e.g., water), which is known as the "breathing effect."\textsuperscript{54,55} PXRD also confirmed that our MIL-53 samples were highly crystalline without any detectable impurity phases. The PXRD patterns showed the complete absence of BDC peaks, which were clearly present in all of the as-synthesized materials (Figure S3). Thus, excess linker molecules (BDC) were completely removed during the hot/warm DMF extraction step of the activation process. SEM images of DMF-extracted and activated materials (Figures 1b−i and Figure S3) show no apparent change in crystal morphology and size after the extraction step and after complete activation. Moreover, the crystal morphologies and sizes were similar to those seen in small batch syntheses.\textsuperscript{27,28,34−36} The BET surface areas and micropore volumes are shown in Table 1, with error bars obtained from three independent samples. These values are comparable to or even higher than the previously reported values,\textsuperscript{27,28,34−36} indicating that high-quality materials were synthesized. The increased surface area could be due to the improvements in the activation protocol of MIL-53s, particularly for MIL-53(Al/
Cr/Ga). As observed previously, MIL-53(Fe) and MIL-53(Sc) did not physisorb nitrogen at 77 K.

The xylene adsorption characteristics of four different MIL-53 materials were initially probed using single-component/unary vapor adsorption isotherms at 323 K (Figure 2). The step in the adsorption isotherms occurs at the transition between the NP and the LP structures. The transition pressure and the saturation capacity are different for each adsorbate and also differ between materials. MIL-53(Sc) demonstrated an essentially nonporous structure with no significant NP → LP transition, and the two xylene isotherms (mX and oX) collected for this material showed negligible adsorption (Figure S4, Supporting Information). MIL-53(Al) has the highest gravimetric oX saturation capacity (4.5 mmol/g) and the lowest transition pressure for oX uptake. MIL-53(Fe) shows the lowest transition pressures for pX adsorption, but the highest pX capacity is exhibited by MIL-53(Al). MIL-53(Fe) had the highest mX capacity at saturation but had the most difficulty in reaching the NP → LP transition. Even after the transition pressure was reached, isotherm collection took an unusually long amount of time, indicating that the structure may not have fully reached the LP form. The EB capacity is consistently the lowest among all if the C₈ isomers in all four materials.

Computational investigations were then conducted on unary C₈ aromatics adsorption in MIL-53 to predict the effects of framework flexibility. First, GCMC calculations were carried out to obtain unary isotherms for all four adsorbates in rigid LP structures of MIL-53(Al). Figure 3a shows the results for MIL-53(Al), whereas the results for the other three materials are shown in Figure S5 (Supporting Information). With the rigid structure approximation, the simulations show poor agreement with the experimentally obtained uptake pressures and adsorption capacities. It has been reported that it is critical to account for the different flexibility modes (NP → LP breathing and lattice expansion effects) of MIL-53 while simulating adsorption properties. To account for the NP → LP breathing, OFAST calculations were performed. It was found that C₈ aromatics do not adsorb in the NP structures of MIL-53 at 323 K. Previous studies have reported nonzero adsorption in the NP structure, leading to two-step isotherms for xylene adsorption in MIL-53(Al) at 383 K. However, it is also reported that the two-step isotherms in MIL-53(Al) are replaced with a one-step isotherm at lower temperatures. XRD patterns indicate that the MIL-53 adsorbents are in the NP structure initially, which have essentially zero adsorption capacity at 323 K. At a certain pressure, the NP → LP transition results in a high uptake as observed in the unary isotherms. Adsorption isotherms in both pore structures were then calculated using GCMC for all of the MIL-53 adsorbents and then combined using the OFAST method. Other than breathing, MIL-53 adsorbents are also known to expand to a certain extent at high loadings of xylene isomers. It has been reported that the unit cell volumes of MIL-53 and MIL-47 increased at high loadings of xylene isomers. To model this flexibility, the adsorbate-loaded frameworks obtained from GCMC simulations were relaxed with MD using fully bonded force fields. GCMC simulations were then performed using the MD-relaxed structure, and GCMC+MD simulations were iteratively carried out to obtain converged lattice parameters (Table S7, Supporting Information) and adsorption capacity of each C₈ isomer. After accounting for both the breathing and the swelling modes of MIL-53 framework flexibility, the predicted unary isotherms are in much closer agreement with the experimental data (Figure 3b and Figure S5). The simulated uptake pressures shift by about 5 orders of magnitude and come into good agreement with the experimental observations. The simulated capacities for all adsorbates also increased. The EB adsorption capacities show the largest differences with the experiments, possibly because the MIL-53 structural transitions occur more slowly in the presence of EB and thus the experimental EB adsorption isotherms may not have reached saturation even at long times. A detailed comparison of the computational and experimental saturation capacities is shown in Table S8 (Supporting Information). For all of the materials, the simulations predict that oX has the highest adsorption capacity followed by pX and then mX, in agreement with experiments and with previous studies performed on MIL-53(Al). Among all of the frameworks, both the experimental and the simulation results...
point to MIL-53(Al) having the highest adsorption capacity for each adsorbate.

We then performed quaternary liquid breakthrough measurements on three of the materials: MIL-53(Al), MIL-53(Cr), and MIL-53(Ga). We excluded MIL-53(Fe) from this study since it showed significantly lower unary saturation capacities (Table S8). C8 aromatics separation is typically conducted in the liquid phase at higher pressures (~100 psi), and the observed unary characteristics of MIL-53(Fe) would likely limit its separation performance. Figure 4 shows the results of liquid breakthrough measurements for each of the three MIL-53 materials. It is evident that all of the MIL-53 adsorbents investigated are oX selective, with MIL-53(Al) being the most selective among the three. The TIPB tracer breakthrough is much faster than that of the C8 aromatics, since it is very weakly adsorbed. A careful observation of Figure 4 also reveals that in MIL-53(Cr) and MIL-53(Ga) some separation of pX and mX can be achieved with breakthrough occurring in the following order: EB < pX < mX < oX. However, in MIL-53(Al), there is insignificant relative separation of pX and mX with the relative order of breakthrough times EB < pX ≈ mX < oX. The “roll-up” effect is also observed in all the three adsorbents studied, with the greatest effect occurring in MIL-53(Al) (Figure 4a). In all of the materials, the roll-up effect is synchronous with the breakthrough of oX, indicating that the more strongly adsorbing oX displaces the initial adsorbed pX, mX, and EB from the MIL-53 pores. In order to obtain quantitative information from the breakthrough data, the roll-up effects as well as the variations in the outlet flow rate must be taken into account when calculating the adsorbed amounts of each component. The time-dependent outlet liquid flow rates (and also the pressure drop) are recorded for each MIL-53 column. Figure S6 (Supporting Information) shows typical data from a MIL-53(Al) column. The flow rate data in Figure S6 are used to obtain the time-dependent flow velocity when integrating eq 1.

Quantitative values of selectivity and capacity were obtained from the experimental data and are depicted in Figure 5. A detailed listing of the obtained values is given in Table S9. The oX selectivity relative to all other components combined ("oX/All") of MIL-53(Al) is around 5, while MIL-53(Cr) gives a selectivity of 3, and MIL-53(Ga) leads to a selectivity of 2.5. There is no statistically significant difference between the oX/pX and the oX/mX selectivities of MIL-53(Al), the mean values of which were computed to be 5.2 and 5.1, respectively. This is in agreement with previous work on MIL-53(Al) that reports no relative pX and mX selection in this adsorbent from binary liquid-phase breakthrough experiments. However, MIL-53(Cr) and MIL-53(Ga) both show a significant mX/pX selectivity of around 1.4. The oX/EB selectivity in MIL-53(Cr) is 4.9, which is much less than MIL-53(Al), where it is around 8. In terms of overall capacities, MIL-53(Cr) (4.9 mmol/g) is similar to that of MIL-53(Al) (4.6 mmol/g). MIL-53(Ga) had the lowest overall capacity of 3.4 mmol/g. This is consistent with its smaller BET surface area even when accounting for the different framework densities of the MOFs due to their different metal centers (Table 1). In terms of the oX capacity, MIL-53(Al) had the highest value (3 mmol/g).

The above findings clearly point to the dominance of competitive oX adsorption over the other isomers in all of the MIL-53 series of adsorbents under industrially relevant conditions (liquid phase, higher pressure, quaternary mixture) regardless of the saturation loadings and uptake pressures observed in single-component adsorption. Although oX selectivity in the MIL-53 series has been reported previously using binary liquid-phase breakthrough experiments for MIL-53(Al) and MIL-53(Fe), the present work is the first to carry out quaternary liquid breakthrough measurements with industrially relevant xylene mixture compositions and
adsorption conditions. The observation that MIL-53(Al) cannot discriminate between mX and pX has been made in previous literature reports, but here it is interesting to observe that both MIL-53(Cr) and MIL-53(Ga) adsorb mX preferentially over pX in multicomponent breakthrough. The breathing behavior of the adsorbents in the MIL-53 series with respect to temperature or humidity is different due to the known effect of the metal center on the adsorbent–adsorbate interactions. We independently verified the effect of different metal centers on the temperature-induced NP → LP transitions of the three adsorbents by in situ XRD under nitrogen flow (Figure S7, Supporting Information). Our results show that MIL-53(Al) transforms to the LP form around 348 K, but in MIL-53(Cr) this transformation happens closer to 473 K. In MIL-53(Ga) the material undergoes an incomplete NP → LP transition even when heated to over 573 K, clearly proving that different metal centers in the MIL-53 series can lead to dissimilar overall observed effects.

We now comment upon the oX selectivity in MIL-53(Al) obtained in this work relative to those reported in the two previous studies. In one of the previous works, separate binary batch adsorption measurements from a liquid-phase feed (0.014 M concentration of each of the two isomers in hexane) led to the following selectivities: oX/EB = 10.9, oX/pX = 3.5, and oX/mX = 2.7. However, the authors also reported that whereas in unary adsorption both oX and pX displayed 40–45 wt % uptake in MIL-53(Al), in equimolar binary mixtures oX dominated the adsorption (up to 45 wt % uptake) while pX never exceeded more than 5 wt % uptake. The authors predicted an increasing binary oX/pX selectivity with increasing bulk-phase liquid concentrations, with selectivity up to 12 at 0.6 M bulk concentration of each isomer.

In this study, multicomponent breakthrough runs were conducted at an oX isomer concentration of 1.8 M, so it is reasonable that we obtain higher selectivity values than those previously reported from binary batch measurements at 0.014 M and comparable selectivities to the previous measurements at 0.6 M. In another previous work, ternary breakthrough measurements for oX, pX, and mX have been reported in MIL-53(Al) at 313 K and 2.7 M equimolar bulk isomers concentrations in heptane. The authors used MIL-53(Al) pellets (also containing binders) that were supplied by BASF. They reported a low oX/pX selectivity of ∼2 and justified this value by hypothesizing that the binder may have prevented the full NP → LP breathing and/or caused pore blockage. Compared to the reported BET surface area (550 m²/g) of MIL-53(Al)/binder pellets used in their work, our samples of pure MIL-53(Al) have a much higher BET surface area (Table 1).

To complete our experimental study in this work, we investigated the long-term stability and performance of the MIL-53 adsorbents. We first performed a stability test by immersing the adsorbents (in both powder and pelletized forms) in a C₈ isomer mixture for up to 30 days (see Methods section) and then characterizing the recovered adsorbents. We use the BET surface area and micropore volume as markers of the adsorbent stability. Figure 6a shows the evolution of textural characteristics in MIL-53(Al), Figure S8 shows the corresponding data for MIL-53(Cr) and MIL-53(Ga), and Table S10 shows the detailed numerical values of BET area and micropore volume obtained in these experiments. All of the MIL-53 adsorbents are seen to be stable in the C₈ aromatic isomer mixture, with both powder and pelletized MIL-53 samples showing stable BET area and micropore volume over the entire 30 days of immersion. A minor decrease of 10–20% in BET area and micropore volume is seen in the first 7–15 days, but these quantities remain stable (or slightly increase) in the next 15 days. Among the three MOFs, MIL-53(Cr) and MIL-53(Al) showed essentially the same stability whereas MIL-53(Ga) showed somewhat more loss of porosity in the initial exposure period (Figure S8). This data also demonstrates that under the pelletization pressures used in this work (1000–2000 psi) there is little difference in the textural characteristics of the pellets versus the unpelletized powders. The preservation of crystal structure of all of the materials was also confirmed by XRD after pelletization and after the stability tests (data not shown). Having confirmed the long-term stability under static immersion conditions, we studied the dynamic cycling performance of MIL-53(Al)—the most oX-selective material—via four breakthrough adsorption–desorption cycles carried out over a period of more than 2 days. The results (Figure 6b) indicate no significant changes in the oX selectivity and total capacity of MIL-53(Al) during the cycling.

Figure 5. (a) oX selectivity (relative to each of the other components and relative to all other components); (b) adsorption capacity (by each component as well as total) for MIL-53(Al), MIL-53(Cr), and MIL-53(Ga) as obtained from quaternary liquid breakthrough measurements at 323 K and 100 psi.
experiments. The consistency in the capacity values over several cycles also indicates satisfactory performance of hexane in removing the adsorbed C8 aromatics during the desorption phases. This was further confirmed by calculations based upon a desorption run on MIL-53(Al) shown in Figure S9. On desorbing a xylene-saturated MIL-53(Al) column using hexane, the calculated desorption selectivities closely matched experimental adsorption selectivities with a oX/pX selectivity of 5.3 (Table S11).

Multicomponent (quaternary) adsorption simulations were then performed accounting for MIL-53 framework flexibility in order to predict the experimentally observed behavior. This is the first attempt in the literature to study multicomponent adsorption of C8 aromatics in MIL-53 while taking the adsorbate–framework structural coupling into account. Since the multicomponent adsorption occurs at high pressure and high loadings, the MIL-53 frameworks are already in their LP form and consideration of the NP → LP transition is not necessary. However, the LP framework swelling/relaxation at high loadings must be accounted for. In our unary adsorption simulations described earlier in this paper, we used iterative GCMC+MD calculations to describe this effect. It proved very difficult to obtain converged results using the same method for multicomponent adsorption. To simplify the calculations, it was proposed that the relaxation of MIL-53 LP structures due to adsorbates at high loading is not significantly dependent on the type of adsorbate among the C8 aromatic isomers, even though it is significantly different compared to the empty structure. This is initially supported by the fact that the relaxation of frameworks in single-component studies shows that the increase in volume due to adsorbate loading is similar for all C8 aromatics. To test this hypothesis further, histograms of the linker dihedral angle were plotted for MIL-53(Al) loaded with each of the four adsorbates (Figure S7). The linker dihedral angle is the dihedral C1–C2–C3-O2 in MIL-53 (Figure S2), which represents the rotation of the BDC linker during the molecular dynamics simulations. Similar histograms for MIL-53(Cr) and MIL-53(Ga) are shown in Figure S10. It is seen that the linker dihedral angle distribution is not significantly dependent on the type of C8 aromatic adsorbate. Note that the dihedral distribution is significantly different in the empty framework as compared to the adsorbate-loaded frameworks. The above findings allow a simplification in modeling the flexibility of MIL-53 during multicomponent adsorption. Dynamical snapshots of each relaxed MIL-53 framework containing oX at high loading were generated using NPT MD simulations in order to describe the adsorbate–framework structural coupling. The adsorption properties of C8 aromatics were then calculated using GCMC simulations for 10 distinct snapshot structures and averaged to obtain physically realistic values.

A detailed comparison of experimental and computational multicomponent capacities and selectivities for the three MIL-53 adsorbents is given in Table S9. Figure 8 shows comparisons between four computed selectivities (oX/mX, oX/pX, oX/EB, and oX/All) versus those obtained experimentally in this work. For MIL-53(Al), data from the two previous experimental works3,4 are also shown for comparison, even though they were obtained only for binary mixtures as discussed earlier. In general, the simulations are in qualitative agreement with our experimental data. The total capacities (Table S9) are in good agreement (2−20% difference between experiment and simulation). In Figure 8, the four selectivities show the same trends in experiment and simulation, with oX/EB selectivities being the highest. Both simulations and experiments concur that MIL-53(Al) has the highest oX selectivity among all MIL-53 adsorbents and that all MIL-53 series of adsorbents are oX selective. Quantitatively speaking, the simulations are seen to underpredict the selectivities. A previous report21 explained the oX-selective nature of MIL-
Methyl groups in oX are at adjacent positions, allowing the interaction of both methyl groups with the carboxylate groups of the MIL-53 framework, whereas mX and pX molecules can only interact with carboxylate groups via one methyl group. The methyl group in the meta position of mX can interact with carbon atoms of the aromatic ring of the framework, but the geometry of pX prevents the interaction of the para-methyl group with the framework. This theory supports the selectivity order of xylene isomers observed in MIL-53. However, the adsorption energies of C₈ aromatics calculated by our GCMC simulations are not found to be significantly different (oX, −60.7; mX, −59.53; pX, −59.45; EB, −59.1 kJ/mol). Another author suggested that the oX-selective nature of MIL-53(Al) is related to the dynamic rotation of the organic linker in the MIL-53 framework and its sensitivity to the type of aromatic isomer adsorbate. However, our MD calculations (Figure 7) show that the distribution of linker rotation angle is not significantly different for the different isomers. Rather, the high experimental oX selectivity observed in multicomponent liquid breakthrough, the roll up effects showing preferential oX adsorption at high xylene loadings, and a lack of correlation of multicomponent oX selectivity (Figure 5) with unary oX capacities (Table S8) lead us to hypothesize that entropic effects such as better packing efficiency of oX under high xylene loadings—along with preferred interactions of oX with the MIL-53 framework—lead to the observed oX selectivity. It is also worth mentioning that while the activated MIL-53 materials did have slight differences in crystal size (~1 µm) due to the different synthesis approaches employed, under the pelletization pressures (1000−2000 psi) used in this work, all pellets generated had similar textural properties (Table S10). Furthermore, all generated pellets were sieved to yield uniform 200−400 µm particle sizes. Thus, macroscopic effects such as differences in crystal size and pellet morphology are not the cause of the observed differences between the MIL-53 materials.

**CONCLUSIONS**

We investigated C₈ aromatic isomer adsorption and separation by different members of the flexible MIL-53 MOF series via a combined experimental and computational methodology. The inclusion of flexibility effects in adsorption simulations through the use of OFAST methods was found to be effective in correctly predicting unary C₈ isomer adsorption in several MIL-53 materials. Quaternary liquid-phase breakthrough measurements showed all of the MIL-53 adsorbents to be oX selective. MIL-53(Al) showed the highest oX selectivity, while both MIL-53(Cr) and MIL-53(Ga) showed significant mX/pX separation unlike MIL-53(Al). Though previous reports exist on the oX selectivity of MIL-53(Al) and MIL-53(Fe), this work is the first to report quaternary liquid-phase breakthrough measurements in MIL-53 materials under industrially relevant xylene feeds and operating conditions. Furthermore, we report the first simulations of C₈ aromatic isomer multicomponent adsorption in MIL-53, and the results are shown to be in good qualitative agreement with experiment. Upon the basis of consideration of all our results, it appears that both the packing efficiency of oX in MIL-53 under high xylene loadings as well as its preferential interaction with the linker determine the observed oX selectivity in MIL-53 materials.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b09105.

MIL-53 synthesis recipes, schematic of the liquid breakthrough apparatus, details of OFAST simulations, force field parameters for MD calculations, DFT-optimized lattice parameters for MIL-53 adsorbents, PXRD patterns and SEM images of MIL-53 adsorbents, S3(Al) as being due to preferred interactions of C₈ aromatics with the MOF framework. Methyl groups in oX are at adjacent positions, allowing the interaction of both methyl groups with the carboxylate groups of the MIL-53 framework, whereas mX and pX molecules can only interact with carboxylate groups via one methyl group. The methyl group in the meta position of mX can interact with carbon atoms of the aromatic ring of the framework, but the geometry of pX prevents the interaction of the para-methyl group with the framework. This theory supports the selectivity order of xylene isomers observed in MIL-53.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: sankar.nair@cbhe.gatech.edu.
*E-mail: david.sholl@cbhe.gatech.edu.
*E-mail: krista.walton@chbe.gatech.edu.

ORCID
Krista S. Walton: 0000-0002-0962-9644
David S. Sholl: 0000-0002-2771-9168
Sankar Nair: 0000-0001-5339-470X

Author Contributions

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. M.A, S.B, and Y.H contributed equally.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by ExxonMobil Chemical Co. We acknowledge M. Barroso, Y. Chiang, and R. Verploegh (Georgia Tech) for assistance in conducting MOF synthesis, in situ XRD measurements, and molecular dynamics simulations, respectively.

■ REFERENCES


