1. Introduction

Metal-organic frameworks (MOFs) consisting of organic linker such as terephthalic acid or fumaric acid and cation such as Al\(^{3+}\) or Zr\(^{4+}\) were prepared by the hydro- and solvo-thermal methods. MOFs were characterized by XRD, N\(_2\) adsorption-desorption isotherm and FE-SEM. The prepared MOFs were mostly crystalline and phase-pure. MOFs were used as the column packing for chromatographic separation of \(p\)-xylene from a xylene mixture. With MOFs prepared with large linker molecules, xylenes diffused into the micropores and eluted fundamentally according to kinetic molecular size. With MOFs of low crystallinity or very small micropores, xylenes passed through spaces between MOF particles and separation of \(p\)-xylene was not possible. With MOFs consisting of fumaric acid and Zr\(^{4+}\) (MOF-801), \(o\)- and \(m\)-xylenes eluted quickly and \(p\)-xylene eluted later, because \(o\)- and \(m\)-xylenes passed through spaces between MOF particles, whereas \(p\)-xylene diffused into the micropores of MOF-801. Temperature dependence of separation with MOF-801 revealed that at temperatures lower than 140 °C, xylenes could not diffuse into the micropores. At 170 °C, the smallest \(p\)-xylene diffused into the micropores and thus \(p\)-xylene could be separated from \(o\)- and \(m\)-xylenes by the molecular-sieving mechanism. MOF-801 was robust against repeated exposure to xylenes and heat treatment at high temperature for elution of adsorbed xylene.

**Keywords**
- \(p\)-Xylene separation, Metal-organic framework, Molecular sieve, Temperature effect, Structural stability

MOFs have been investigated for the separation of xylenes\(^{15\text{-}25}\). In most cases, xylenes diffused into the micropores and separation was governed by the diffusion rate based on the molecular size of xylenes or by interactions between the MOF surface and xylenes. The separation mechanism is similar to that of the conventional process using zeolite, so the required volume of adsorbent is large because all the xylene substrate...
diffuses into the micropores. Therefore, MOFs should be identified that absorb only \(\text{p-xylene}\) to reduce the necessary amount of MOF, thus reducing the costs of adsorbent and plant equipment.

The present study prepared MOFs with micropores in a suitable range for evaluation in the vapor-phase chromatographic separation of \(\text{p-xylene}\) from mixed xylenes and ethylbenzene, especially to operate as a molecular sieve. Promising MOFs were screened from MOFs with various pore sizes and then the separation mechanism was studied with the selected MOFs.

2. Experimental

2.1. Preparation of MOFs

Typically, 35.0 mmol of \(\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}\), 17.5 mmol of terephthalic acid (TPA) and 50 cm\(^3\) of distilled water were placed in a 50 cm\(^3\) glass beaker and the mixture was stirred for 10 min with a magnetic stirrer. The mixture was transferred into an autoclave with Teflon lining. The autoclave was placed in an oven at 220 °C and held at this temperature for 72 h. The autoclave was cooled to room temperature and the solid product was separated by centrifugation at 5000 rpm for 10 min. The product was washed with distilled water and then \(N,N\)-dimethyl formamide (DMF) to remove unreacted TPA. The product was washed with acetone to remove DMF. After centrifugation, the product was dried at 250 °C overnight under reduced pressure of 10 hPa to obtain TPA-Al\(^{26}\). The final product was 2.49 g (theoretical yield 3.18 g). In this case, TPA is the linker and Al is the corner cation. Similarly, using various linkers, cations and solvents under appropriate synthesis conditions, various MOFs were prepared as in Table 1\(^{26-36}\).

2.2. Characterization

Crystal structure was analyzed by X-ray diffraction spectroscopy (XRD; Rigaku Corp., RINT 2000) using Cu Kα radiation at 40 kV and 20 mA. The specific surface area and pore-size distribution were measured by conventional N\(_2\) adsorption-desorption isotherm analysis (MicrotracBEL Corp., BEL-mini). Specific surface area was calculated by the BET method. Pore-size distributions were calculated by the BJH method for the mesopore region, and the MP method, SF method or HK method for the micropore region. Before the measurement, the materials were dried at 250 °C for 1 h under a N\(_2\) stream. Morphology of the MOF particles was observed with field-emission scanning electron microscopy (FE-SEM; JEOL Ltd., JSM-6700) at 10 kV and 10 \(\mu\)A.

| MOF        | Source [mmol] | Cation | Linker Source [mmol] | Modulator [mmol] | Solvent Temp. Time [cm\(^3\), °C, h] |
|------------|---------------|--------|----------------------|------------------|--------------------------------------|
| TPA-Al\(^{26}\) | Al(NO\(_3\))\(_3\)·9H\(_2\)O | 35.0   | Terephthalic acid (TPA)| 17.5             | H\(_2\)O 50 220 72                  |
| FMA-Al\(^{27}\) | Al(NO\(_3\))\(_3\)·9H\(_2\)O | 7.4    | Fumaric acid (FMA)   | 12.6             | DMF 17.2 130 17                     |
| isoPA-Al\(^{28}\) | Al\(_2\)(SO\(_4\))\(_3\)·18H\(_2\)O | 6.0    | Isophthalic acid (isoPA) | 6.0              | H\(_2\)O 50 135 12                  |
| FMA-Fe\(^{29}\) | FeCl\(_3\)·6H\(_2\)O | 10.0   | FMA                  | 10.0             | DMF 50 100 12                       |
| FMA-Ti\(^{30}\) | TiCl\(_4\) | 2.6    | FMA                  | 7.8              | DMF 20 120 24                       |
| FMA-Zr\(^{30}\) | ZrCl\(_4\) | 2.6    | FMA                  | 7.8              | DMF 20 120 24                       |
| TPA-Zn\(^{31}\) | Zn(NO\(_3\))\(_2\)·6H\(_2\)O | 4.0    | TPA                  | 2.0              | DMF 40 120 6                        |
| TPA-Zr\(^{32}\) | ZrCl\(_4\) | 8.4    | TPA                  | 8.4              | DMF 20 200 12                       |
| BDA-Zr\(^{33}\) | ZrCl\(_4\) | 1.4    | 4,4'-Biphenyldicarboxylic acid (BDA) | 1.4              | DMF 20 120 24                       |
| NDA-Zr\(^{34}\) | ZrCl\(_4\) | 2.6    | 1,4-Naphthalenedicarboxylic acid (NDA) | 2.6              | DMF 20 120 24                       |
| PDA-Zr\(^{35}\) | ZrCl\(_4\) | 1.8    | 3,5-Pyrazoledicarboxylic acid (PDA) | 1.5              | DMF 20 120 24                       |
| TrimesicA-Zr\(^{36}\) | ZrCl\(_4\) | 2.6    | Trimesic acid (TrimesicA) | 2.6              | DMF 20 120 24                       |
| MesaconicA-Zr\(^{37}\) | ZrCl\(_4\) | 2.6    | Mesaconic acid (MesaconicA) | 7.8              | DMF 20 120 24                       |
| CycloA-Al\(^{38}\) | Al\(_2\)(SO\(_4\))\(_3\)·6H\(_2\)O | 2.0    | 1,4-Cyclohexanedicarboxylic acid (CycloA) | 3.0              | DMF 30 100 54                        |

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chromatograph. Helium was fed as a carrier gas at 15 cm³ min⁻¹ (STP). At first, MOF was pre-treated in-situ at 200 °C for 1 h before pulse injection of 0.20 to 2.0 µL of each probe molecule or a mixture of xylenes with a microsyringe. Temperatures at the injection port and detector were 220 °C and column temperature varied between 100 °C and 220 °C. Retention time (peak top time) was used for the following analyses.

To confirm the purity of p-xylene, the effluent gas at the exit of the gas chromatograph was collected into a heptane trap (1 cm³). The trapped liquid was analyzed with a gas chromatograph with flame ionization detector equipped with InertCap Pure-WAX column (length 30 m, film thickness 0.25 µm, I.D. 0.25 mm).

3. Results and Discussion

3.1. Characterization of MOFs and Separation of Xylenes and Ethylbenzene with MOFs

Table 2 summarizes the characteristics of the MOFs and the properties for separation of xylenes and ethylbenzene (EB).

Most MOFs were highly crystalline except for FMA-Ti, FMA-Fe and TPA-Zn. FMA-Ti was amorphous and FMA-Fe did not contain the reported MOF structure. TPA-Zn showed the main peaks of MOF-5 in the low-angle region, but the peaks in the high-angle region were broad and peak resolution was low. The XRD pattern of FMA-Al was fair and FMA-Al contained a small amount of impurity. TPA-Al contained boehmite as an impurity.

Separation properties were categorized into three types. MOFs of Category 1 showed elution of xylenes and EB at the same time of ca. 0.2 min. A representative chromatographic trace is shown in Fig. 1. PDA-Zr had a small surface area based on adsorption of nitrogen, which suggests that even nitrogen could not diffuse into the pores of PDA-Zr. Therefore, xylenes and EB passed through the space between PDA-Zr particles. This phenomenon was also observed for TPA-Zn and FMA-Fe. Thus, separation of p-xylene was not possible using MOFs of Category 1.

MOFs of Category 3 showed longer and variable elution times for xylenes and EB. A representative chromatographic trace is shown in Fig. 2. Most Category 3 MOFs showed higher diffusion rate in the micropores for p-xylene with the small kinetic diameter and lower diffusion rate for o-xylene with larger kinetic diameter. Elution time was 8 min for TPA-Zr. Much longer times were necessary for xylenes and EB to pass through the micropores of FMA-Al, probably because the micropores were small compared with that of terephthalic acid or trimesic acid. The order of elution was different for the MOFs, so not only the size of the micropores but also the interactions between MOF and xylenes and EB may have influenced the diffusion rate.

Separation of xylenes can be discussed based on Henry’s constant. Henry’s constant depends on

Table 2 Properties of MOFs and Separation of Xylenes and Ethylbenzene

| Category | MOF       | XRD                  | BET   | Pore diameter | SEM            | Elution time |
|---------|-----------|----------------------|-------|---------------|----------------|--------------|
|         |           |                      | [m² g⁻¹] | [nm] | aggregate     | 15 cm³ min⁻¹ | [min]        |
| 1       | PDA-Zr    | good                 | 50    | 0.6, 0.8      | aggregate 0.2 m   | 0.2 EB       |
|         | TPA-Zn    | poor                 | 120   | 0.6           | aggregate 0.2 m   | 0.2 EB       |
|         | FMA-Zn    | poor                 | 210   | 0.6           | 18 hedron 0.2 m   | 0.2 EB 0.3   |
|         | CycloA-Al | good                 | 400   | 0.6           | no data          | 0.2 EB 1.1   |
| 2       | TPA-Zr    | good                 | 740   | 0.6           | truncated cubic 0.2 m | 2.0 EB 2.0 | EB 3.6 |
|         | FMA-Zr    | good                 | 860   | 0.6           | cubic            | 0.3 m 0.6 EB 0.6 | 0.7 |
| 3       | TPA-Al    | good, small amount of boehmite | 420 | 0.6, 3.8 | plate EB 0.4 | 0.5 m 0.8 | 2.7 |
|         | isoPA-Al  | good                 | 560   | 0.6, 3.8      | aggregate 1.1 m   | 1.2 EB 1.2   |
|         | TrimesicA-Zr | good                  | 1420  | 0.7           | spherical 1.2 m   | 2.0 EB 2.0   |
|         | TPA-Zr    | good                 | 740   | 0.6           | aggregate 2.9 m   | 3.6 EB 4.5   |
|         | BDA-Zr    | good                 | 1530  | 0.6           | aggregate 3.5 m   | 3.9 EB 0.4  |
|         | NDA-Zr    | good                 | 1120  | 0.6, 3.9      | aggregate 5.3 m   | 5.5 EB 0.9   |
|         | FMA-Al    | fair, small amount of impurity | 1440 | 0.6 | aggregate 7.8 m | 9.2 EB 20 | 24.7 |

a) Instrumental limitation: 0.6 nm. b) o-, m-, p-xylenes and ethylbenzene (EB), column temp.: 170 °C, injection: 0.2 µL.
the specific MOF so that discussion is not simple. For example, the order of Henry’s constants for \( o \)-, \( m \)- and \( p \)-xylene was \( \text{ortho} > \text{meta} > \text{para} \) for Zn(BDC) (DABCO). Here, BDC denotes terephthalic acid and DABCO denotes 1,4-diazabicyclo[2.2.2]octane\(^{25}\). On the other hand, the order was \( \text{para} > \text{ortho} \approx \text{meta} \) for FMA-Al\(^{24}\). Thus, Henry’s constants must be measured for FMA-Zr and the measurement will be carried out in the near future.

MOFs of Category 2 showed different elution behavior from those of Categories 1 and 3, as \( o \)- and \( m \)-xylene eluted quickly at ca. 0.2 min and subsequently a small peak for \( p \)-xylene appeared. A representative chromatographic trace is shown in Fig. 3. This suggests that \( p \)-xylene passed through the micropores and \( o \)- and \( m \)-xylene of larger kinetic diameters passed through spaces between the MOF particles. These findings suggest that xylenes could be separated by the molecular-sieving mechanism with Category 2 MOFs. This is very important for the separation of \( p \)-xylene from a xylene mixture. Injection of the xylene mixture (\( \text{ortho} : \text{meta} : \text{para} = 1 : 1 : 1 \) molar ratio) found the same behavior (Fig. 4); \( o \)- and \( m \)-xylene gave one immediate peak. Increase of the column temperature from 170 to 200 °C resulted in elution of \( p \)-xylene. Thus, separation of \( p \)-xylene from the xylene mixture was possible. If the pseudo-transfer bed were adopted, pure \( p \)-xylene could be obtained by switching the flow, as now adopted for the industrial separation of xylenes\(^{13}\). The adsorbent now used industrially is X-type zeolite, so every xylene molecule is contained in the zeolite micropores, suggesting the necessity for a large micropore volume to accommodate the total xylene. On the other hand, only \( p \)-xylene diffuses into the micropores of FMA-Zr, so the necessary amount of MOF is smaller than that of zeolite. Consequently, the separator becomes smaller; probably one third or one fourth of the size now used considering the pore volumes of adsorbents and the molar ratio of xylenes in an industrial process (\( \text{ortho} : \text{meta} : \text{para} = 1 : 1-2 : 1 \)), which reduces the investment and separation cost.

The purity of \( p \)-xylene was confirmed by collecting the effluent gas from the gas chromatograph outlet in the heptane trap. The collected effluent solution after 2 min in Fig. 4 was analyzed with a capillary gas chromatograph. The purity of collected \( p \)-xylene was 77% with \( m \)-xylene 19% and \( o \)-xylene 4% from a 1 : 1 : 1 mixture of xylenes. Purity of \( p \)-xylene could be improved by adopting the optimum separation temperature (see below).

### 3.2 Effect of Separation Temperature

Previously, vapor phase separation has been the main focus of investigation, but separation in the liquid phase does not involve the energy for vaporization of xylenes. Consequently, we investigated the liquid phase separation of xylenes as follows. Three xylene isomers were dissolved in 1,3,5-trimethylbenzene and the amount of each xylene was selected to exactly fill the micropores of FMA-Zr (0.25 cm\(^3\) g\(^{-1}\)). FMA-Zr was added at room temperature to the xylene mixture solution. We assumed that the amount of \( p \)-xylene in the solution
would gradually decrease with time. However, small
and similar adsorption was observed for each xylene,
probably because xylenes were adsorbed on the outer
surface of FMA-Zr. This indicated that the tempera-
ture for separation was important; at low temperatures
no xylenes would be absorbed and at higher tempera-
tures only \( p \)-xylene would be absorbed because the
pore-mouth would expand at higher temperatures to
allow \( p \)-xylene to diffuse into the micropores.

Thus, we investigated the effect of temperature in the
vapor phase. The temperature adopted in section 3.1
was \( 170 \) °C (Fig. 3), and \( \alpha \)- and \( m \)-xylenes had the same
elution time and the peak for \( p \)-xylene was very small
at this temperature, suggesting that \( p \)-xylene remained
in the micropores. All three xylenes eluted almost at the
same elution time at \( 100 \) °C (Fig. 5 (a)). The peak
for \( m \)-xylene at \( 0.2 \) min became smaller at \( 200 \) °C,
which suggests that the pore-mouth expanded due to
thermal vibration of the MOF structure. Furthermore,
this result suggests that fine tuning of the size of the mi-
cropore entrance (aperture) is possible with separation
temperature, which may be useful for other separation
targets. It has been reported that the MOF structure
changes with temperature \(^{39} - ^{41}\), but our result is the
first one to indicate that this effect is useful for separa-
tion processes. Structural changes with adsorption of
\( \text{CO}_2 \) or xylenes are reported \(^{42} - ^{44}\). Adsorption of
\( p \)-xylene caused the structure of MOF to change to ac-
commodate \( m \)- and \( \alpha \)-xylenes, thus losing the selectivity
for \( p \)-xylene \(^{43},^{44}\). This is a severe problem for the
production of low-cost \( p \)-xylene and MOFs with these
properties are inadequate for practical use.

3.3. Stability of FMA-Zr

The stability of FMA-Zr was studied by repeating
pulses at \( 170 \) °C and by heating FMA-Zr at \( 200 \) °C to
elute the adsorbed xylene (Fig. 6). The number be-
side the peak indicates the relative peak area defined as
the peak area divided by the average peak area for three
\( \alpha \)-xylene peaks plus three \( m \)-xyylene peaks.

As discussed above, the peak areas for \( \alpha \)-xylene and
\( m \)-xylene were the same because these xylenes did not
diffuse into the micropores of FMA-Zr but passed
through the space between particles. After six pulses,
three for \( \alpha \)-xylene and three for \( m \)-xylene, \( p \)-xylene was
pulsed eight times. As is clearly seen, the peak form
was very different from those for the other two xylenes.
The amount of FMA-Zr used, 50 mg, and the pore
volume of FMA-Zr, \( 0.25 \) cm\(^3\) g\(^{-1}\), suggest that all \( p \)-xylene
could be adsorbed and no peak would be observed.
However, about 85% of the peak area for \( p \)-xylene was repeatedly observed, suggesting that the balance for diffusion into and passing through the MOF particles was important. Particle size of FMA-Zr might have influenced this phenomenon, which requires further study. After the eight \( p \)-xylene pulses, the temperature was increased to 200 °C and maintained at 200 °C for 30 min to desorb the adsorbed xylenes. The total area for \( p \)-xylene was eight times those for \( o \)-xylene or \( m \)-xylene, suggesting that all pulsed \( p \)-xylene was removed from the FMA-Zr. Then, \( o \)-xylene was again pulsed at 170 °C, which gave identical peak form and peak area as the first \( o \)-xylene pulse. Damage to the structure of FMA-Zr by the adsorption and desorption of xylenes and by the heat treatment up to 200 °C might allow adsorption of \( o \)-xylene resulting in a smaller peak. Thus, FMA-Zr was robust for repeated adsorption of xylene and heat treatment at 200 °C.

4. Conclusions

Crystalline and microporous metal-organic frameworks (MOFs) consisting of various organic linkers and cations were prepared by the hydro- and solvo-thermal methods and were evaluated for vapor-phase separation of \( p \)-xylene from a xylene mixture. MOFs could be categorized into three types based on the chromatographic separation behavior of xylenes and ethylbenzene. Xylenes and ethylbenzene could not diffuse into the MOF micropores with too small pore-mouth and all molecules eluted at the same elution time. Larger pore-mouth allowed all molecules to diffuse into the micropore, but typically smaller molecules like \( p \)-xylene eluted earlier and larger molecules like \( o \)-xylene eluted later. MOFs with a critical pore-mouth size such as MOF-801 formed of fumaric acid and \( \text{Zr}^{4+} \) showed peculiar behavior; \( o \)- and \( m \)-xylenes eluted quickly by passing through the spaces between MOF particles and \( p \)-xylene eluted later by diffusing through the MOF micropores. Thus, separation of \( p \)-xylene from a xylene mixture by the molecular-sieving mechanism was observed using MOFs. The temperature for separation was very important. At temperatures lower than 140 °C, xylenes could not diffuse into the micropores of MOF-801. At high temperature such as 200 °C, larger molecules like \( m \)-xylene started to diffuse into the micropores. At the optimum temperature, only \( p \)-xylene diffused into the micropores and \( o \)- and \( m \)-xylene were excluded. This suggests that the MOF structure is not rigid and the micropore mouth size changes with temperature. Repeated pulses of xylenes and elution of adsorbed \( p \)-xylene at higher temperatures showed that MOF-801 was robust during such processes. Adoption of the pseudo-transfer bed with gradient temperature would allow continuous separation of \( p \)-xylene from the xylene mixture.

**Supporting Information**

![XRD Patterns of PDA-Zr, TPA-Zr and FMA-Zr](image1)

Cu Kα, 40 kV, 20 mA.

![Nitrogen Adsorption/Desorption Isotherms of PDA-Zr, TPA-Zr and FMA-Zr](image2)

![Pore-size Distributions of PDA-Zr, TPA-Zr and FMA-Zr](image3)
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要 旨

金属有機構造体を用いた分子ふるい作用によるパラキシレン分離

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テレフタル酸あるいはフマル酸などの有機リンカーと Al³⁺あるいは Zr⁴⁺などのカチオンからなる有機金属構造体（MOF）を、水熱合成法あるいはソルボサーマル合成法により調製した。得られた MOF を XRD, N₂吸着等温線および FE-SEM で解析し、クロマトグラフィーによるキシレン混合物からのパラキシレン分離用の充填剤として用いた。大きなリンカーで調製された MOF では、キシレンはミクロ細孔内を拡散し、基本的に分子運動直径に従って流出した。結晶性の低いあるいは非常に小さいミクロ細孔の MOF では、キシレンが MOF の粒子間の空間を通過し、パラキシレンの分離はできなかった。一方、フマル酸と Zr⁴⁺からなる MOF（MOF-801）では、オルソキシレンとメタキシレンが速やかに流出し、パラキシレンが遅れて流出した。これは、オルソキシレンとメタキシレンが MOF-801 のミクロ細孔に入ることができず、MOF 粒子間の空間を通過し、パラキシレンがミクロ細孔内を拡散したためである。MOF-801 での分離の温度依存性から、140 ℃より低温ではキシレンがミクロ細孔内に拡散できないことが分かった。170 ℃では、最も小さいパラキシレンがミクロ細孔内を拡散し、このためオルソキシレン、メタキシレンからパラキシレンが分子ふるい作用により分離できた。MOF-801 は、キシレンへの繰り返し暴露や吸着したキシレンの高温での除去に対して安定であった。

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