1. Introduction

Metal-organic framework (MOF), also known as Porous Coordination Polymer (PCP), has crystalline and microporous properties similar to zeolites, which are the basis for various applications\(^1\).\(^2\). MOF was first reported in the early 1990’s\(^3\) and the number of studies on MOFs has increased dramatically. Zeolite was first recognized in 1756 and was widely studied in the early 20th century. Zeolites consist of MO\(\text{tetrahedron} (M: \text{typically Si or Al}) \text{and therefore are rigid, inorganic polymer materials}\(^4\). Zeolites have the additional important specific property of ion-exchange. Consequently, zeolites have been used as solid acid catalysts and detergent additives as “softener.” In contrast, MOF typically consists of metals as the corner cation or cluster and organic “linkers.” MOFs contain organic components, so the thermal stability of MOFs is lower than that of zeolites, although some MOFs are stable up to around 400 °C\(^5\). The number of review papers on MOFs continues to increase yearly, with presently more than ca. 400 review papers per year. On the other hand, the number for zeolites reached the highest of 250 in 2008, and since has been decreasing.

More than 20,000 types of MOFs have been reported\(^6\), whereas only 242 types of zeolites are known\(^4\). MOFs are crystalline and microporous, with very high specific surface areas up to 8000 m\(^2\) g\(^{-1}\) by the BET method\(^7\). The pore size ranges from a few angstroms to more than 10 Å (1 Å = 10\(^{-10}\) m) depending mainly on the size of the linkers. Generally, a larger linker gives a larger pore size.

MOFs have been evaluated for gas adsorption\(^8\) and separation\(^9\), separation of heavy metals\(^10\), sensors\(^11\), thermal- and photo-catalysis\(^12,13\), optics\(^14\), drug delivery\(^15\), electro-chemistry\(^16\), biomedical and bioimaging\(^17\), and other functions. MOFs have also been used as the carbon source for thermal- and electro-catalysts after thermal decomposition\(^18,19\). The microporous structure of MOFs is the most important characteristic for industrial uses. However, the cost of MOFs is also very important. The pore size can be controlled by adopting specific linkers usually with functional groups, but the cost tends to drastically increase and makes the use of MOFs difficult. Therefore, balancing the cost and performance becomes crucial.
This review introduces findings for the oligomerization of ethylene\textsuperscript{20}, hydrogenation of unsaturated aldehyde\textsuperscript{21} and diene\textsuperscript{22}, and separation of aromatics\textsuperscript{23} especially $p$-xylene from a xylene mixture\textsuperscript{24} using various MOFs focusing on the specific microporous structures.

2. Ethylene Oligomerization\textsuperscript{20}

$\alpha$-Olefins are important chemicals in industrial use, such as a co-monomer of low-density polyethylene or raw material for the oxo-reaction. Large amounts of $\alpha$-olefins are produced by oligomerization of ethylene. However, this homogeneous catalytic process\textsuperscript{25} forms a wide range of olefins and a specific olefin such as butene or hexene is difficult to obtain. Recently, a novel process to produce 1-hexene from ethylene was commercialized\textsuperscript{26}. Zeolite micropores could be used to suppress the formation of long-chain olefins such as octene and decene and to obtain butene or hexene selectively. However, exclusive incorporation of a single active site seems difficult. We expected that selective dimerization or trimerization could be attained if the reaction proceeded in the micropores of MOF, thus limiting space for formation of larger molecules together with isolated active sites. We synthesized MOF compounds containing Ni-bipyridyl complex units in its micropores and used for the size-selective oligomerization of ethylene.

Ni/bipyridine complex (Ni/BPY(complex)) was prepared from NiCl\(_2\) and 2,2'-bipyridine (bpy). Similarly, the Ni/BPYDC(complex) was prepared from 2,2'-bipyridine-5,5'-dicarboxylic acid (BPYDC) and NiCl\(_2\). This Ni/BPYDC(complex) was reacted with Al(NO\(_3\))\(_3\)-9H\(_2\)O to obtain Ni/BPYDC-Al(MOF). Ni/BPYDC-Ni(MOF) was also obtained from BPYDC and Ni(NO\(_3\))\(_2\)-6H\(_2\)O. Here, BPYDC is the linker and Al or Ni after the linker is the corner cation.

Fourier transform infrared spectroscopy (FT-IR), N\(_2\) adsorption-desorption isotherm, and X-ray diffraction (XRD) analyses revealed formation of the MOF structure. FT-IR spectra suggested disappearance of carboxylic acid and presence of carboxylate in Ni/BPYDC-Al(MOF) and Ni/BPYDC-Ni(MOF). The BET surface area for Ni/BPY(complex) and Ni/BPYDC (complex) were small, 1 m\(^2\) g\(^{-1}\) and 17 m\(^2\) g\(^{-1}\), respectively, whereas that for Ni/BPYDC-Al(MOF) was 350 m\(^2\) g\(^{-1}\). Thermal analysis of Ni/BPYDC-Ni(MOF) and Ni/BPYDC-Al(MOF) showed weight decreases close to those estimated from the formula of 64.8 % and 70.0 %, respectively, which were comparable to the theoretical weight decreases of 69 % and 72 %, respectively.

Et\(_2\)AlCl is often used as a co-catalyst for the Ziegler-Natta system, so the catalytic activity of Et\(_2\)AlCl was found to be inactive in the reaction conditions adopted. Without Et\(_2\)AlCl, no oligomerization occurred on any of the Ni/BPY(complex), Ni/BPYDC (complex), Ni/BPYDC-Al(MOF) or Ni/BPYDC-Ni (MOF), suggesting that reduction of coordinated Ni-Cl species is necessary. Ni/BPY(complex) achieved conversion of ethylene of 43.5 % as shown in Table 1. Selectivity for butenes exceeded 90 % with small amounts of hexene 7.3 % and octene 1 %. Ni/BPYDC-Al(MOF) gave very high ethylene conversion of 99 %. Ni/BPYDC-Ni(MOF) gave lower ethylene conversion than Ni/BPYDC-Al(MOF), but high 1-butene selectivity was obtained, possibly related to the smaller pore size. Oligomerization of ethylene has been studied with Ni-based homogeneous catalysts\textsuperscript{25,27} and with Ni-based heterogeneous catalysts\textsuperscript{28}. Optimization of the ligands resulted in selectivity of butenes higher than 90 % and 1-butene selectivity higher than 60 %. Thus, the combination of Ni and MOF provides an ethylene oligomerization catalyst with high selectivity for linear butenes.

3. Hydrogenation of Cinnamaldehyde and Cross-coupling Reaction\textsuperscript{21}

| Table 1 | Liquid Phase Oligomerization of Ethylene on Ni/MOF Compounds in the Presence of Et\(_2\)AlCl\textsuperscript{a) b) } |
|----------|--------------------------|
| **Conversion [%]** | 1-C\(_2\)H\(_8\) | trans-2-C\(_2\)H\(_8\) | cis-2-C\(_2\)H\(_8\) | C\(_6\)H\(_12\) | C\(_8\)H\(_16\) | Others\textsuperscript{b) } |
| Ni/BPY(complex) | 43.5 | 46.1 | 26.2 | 19.3 | 7.3 | 1.0 | 0.1 |
| Ni/BPYDC-Al(MOF) | 99.2 | 23.4 | 38.9 | 26.8 | 8.9 | 2.1 | 0.0 |
| Ni/BPYDC-Ni(MOF) | 13.4 | 66.1 | 15.9 | 10.7 | 7.3 | 0.0 | 0.0 |

\textsuperscript{a) }Catalyst: 35 \(\mu\)mol as Ni, Et\(_2\)AlCl: 2.45 mL, C\(_2\)H\(_4\): 1.5 MPa, 5 °C, 1 h, Solvent: n-heptane 15 mL.

\textsuperscript{b) }Others: CH\(_4\), CO\(_2\).

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and cross-coupling reactions were investigated over a noble metal-supported MOF consisting of terephthalic acid (TPA) and chromium cation (TPA-Cr)\(^{29}\). Key points were to establish the location of the reaction and the importance of the microporous structure.

Hydrogenation of Cinnamaldehyde and Cross-coupling Reaction

Pd/TPA-Cr and Ru/TPA-Cr catalysts were prepared from TPA-Cr made from Cr(NO\(_3\))\(_3\)-9H\(_2\)O and TPA. The location of noble metals inside or outside the MOF micropores is important, so various noble metal precursors and solvents for impregnation were adopted. For comparison, \(\alpha\)-Al\(_2\)O\(_3\) (\(<1\) m\(^2\) g\(^{-1}\)) and \(\gamma\)-Al\(_2\)O\(_3\) (167 m\(^2\) g\(^{-1}\)) were also used as catalyst supports.

Hydrogenation of cinnamaldehyde in toluene (solvent) was carried out in an autoclave. All Pd/TPA-Cr catalysts used for the reactions were prepared with Pd(NH\(_4\))\(_4\)(NO\(_3\))\(_2\) using water as the impregnation solvent except for a Pd/TPA-Cr catalyst prepared with PdCl\(_2\) and water, indicated in Table 2 as Pd*. To study the location of hydrogenation at Pd outside or inside the micropores of TPA-Cr, the catalyst was poisoned with 1,10-phenanthroline or 4,7-diphenyl-1,10-phenanthroline.

XRD, N\(_2\) adsorption-desorption isotherm, and thermogravimetry-differential thermal analysis (TG-DTA) profile analyses all indicated successful synthesis of TPA-Cr\(^{29}\). Figure 1 shows the transmission electron microscope (TEM) images of TPA-Cr and 3 wt% Pd/TPA-Cr catalysts. Figure 1a) indicates high homogeneity of TPA-Cr throughout the particles. Figures 1b) and 1c) show Pd/TPA-Cr catalysts prepared by impregnation with PdCl\(_2\) in methanol solvent and PdCl\(_2\) in H\(_2\)O solvent, respectively. Pd particles of a few to ca. 100 nm size were detected, suggesting that Pd was present not only in the micro- and meso-pores but also on the exterior of the MOF particles. Figures 1d) and 1e) show Pd/TPA-Cr prepared with [Pd(NH\(_4\))\(_4\)(NO\(_3\))\(_2\)] in H\(_2\)O solvent. These images are similar to Fig. 1a), indicating that Pd is present inside the micro- and meso-pores as very fine particles.

Hydrogenation of cinnamaldehyde (CMA) was studied to assess the effect of the micropores on the selectivity for C=CH and C=O hydrogenation (Scheme 1). Table 2 compares the effect of the supports. Very high activities were obtained irrespective of the Pd source using TPA-Cr as the support. The selectivities for dihydrocinnamaldehyde (HCMA) and dihydrocinnamyl alcohol (HCMO) were similar for all catalysts. These results suggest that CMA could diffuse rapidly in the micro- and meso-pores of TPA-Cr, and the first hydrogenation occurred at the C=CH double bond and not at the C=O double bond even in the early stage of the reaction. Comparison of supported Pd and Ru catalysts found that Pd preferentially hydrogenated the C=CH double bond and Ru preferentially hydrogenated the C=O double bond. Addition of less bulky 1,10-phenanthroline to 3 wt% Pd/TPA-Cr drastically

| Support | Loaded metal \(^{ab}\) | Conv. [%] | Selectivity \(^{ab}\) [%] |
|---------|-----------------|---------|------------------------|
|         | Pd* 22.2\(^{ab}\) | 0.0     | 100.0                  |
| Pd      | 100.0           | 0.0     | 100.0                  |
| Pd      | 26.9\(^{ab}\)   | 0.0     | 100.0                  |
|         | 75.9            | 0.0     | 100.0                  |
|         | 57.3            | 70.7    | 16.1                   |
| Ru      | 89.9            | 0.0     | 90.5                   |
| Ru      | 25.2            | 45.2    | 40.9                   |
| \(\alpha\)-Al\(_2\)O\(_3\) | 64.0     | 0.0     | 83.9                   |

Table 2 Effects of Supports and Noble Metals on Hydrogenation of Cinnamaldehyde \(^{ab}\)

a) Metal loading: 3.0 wt%, Catalyst: 62.5 mg, Cinnamaldehyde: 0.790 g (5.98 mmol), Solvent: triglyme 11.6 g, 65 °C, 6 h, \(P_{H_2}\): 5.0 MPa.

b) [Pd(NH\(_4\))\(_4\)(NO\(_3\))\(_2\), PdCl\(_2\)* and RuCl\(_3\),/\(_2\)H\(_2\)O were used as noble metal sources.

c) CMO: cinnamyl alcohol, HCMA: dihydrocinnamaldehyde, HCMO: dihydrocinnamyl alcohol.

d) \(P_{H_2}\): 1.0 MPa.

e) Metal loading: 0.50 wt%, Catalyst: 125 mg, Cinnamaldehyde: 1.58 g (12.0 mmol), Solvent: triglyme 22.5 g, 100 °C, 6 h, \(P_{H_2}\): 1.0 MPa.
decreased conversion (Table 3). In contrast, addition of bulkier 4,7-diphenyl-1,10-phenanthroline caused relatively small activity loss. Bulky 4,7-diphenyl-1,10-phenanthroline was adsorbed mostly on Pd on the exterior of TPA-Cr, indicating that hydrogenation mainly occurred in the micro- and meso-pores of TPA-Cr. On the other hand, less bulky 1,10-phenanthroline was adsorbed on Pd located both in the micro- and meso-pores and on the external surface. The molecular sizes of 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline were estimated by MOPAC 6.0(30). The major and minor axes of 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline were calculated to be 11.6 Å × 7.9 Å and 14.9 Å × 10.8 Å, respectively. These values suggest that 1,10-phenanthroline can diffuse into the micropores of TPA-Cr and retard the reaction, whereas 4,7-diphenyl-1,10-phenanthroline cannot easily diffuse into the micropores, resulting in less effect on the activity, consistent with the results in Table 3.

To evaluate the effect of the location of Pd on Pd/TPA-Cr on selectivity, the cross-coupling reaction between bromine compounds and phenylboronic acid was studied on Pd/TPA-Cr and Pd/α-Al₂O₃ (Table 4). Yield was always higher on Pd/TPA-Cr than on Pd/TPA-Cr in Table 3.

| Additive | Pd : P or DP [mol : mol] | Conv. [%] | Selectivity [%] |
|----------|--------------------------|-----------|-----------------|
|          |                          |           | CMO | HCMA | HCMO |
| none     |                          | 100.0     | 3.4 | 81.0 | 15.6 |
| P        | 1 : 3                    | 21.5      | 0.0 | 100.0| 0.0  |
|          | 1 : 10                   | 23.3      | 0.0 | 100.0| 0.0  |
|          | 1 : 15                   | 25.0      | 0.0 | 100.0| 0.0  |
| DP       | 1 : 3                    | 73.1      | 0.0 | 76.7 | 22.3 |
|          | 1 : 10                   | 71.4      | 0.0 | 89.3 | 10.7 |
|          | 1 : 15                   | 65.0      | 0.0 | 91.5 | 8.5  |

a) Catalyst: 31.7 mg, Cinnamaldehyde: 0.39 g (3.0 mmol), Solvent: toluene 5.0 g, 65 °C, 3 h, P_H₂: 5.0 MPa.
b) CMO: cinnamyl alcohol, HCMA: dihydrocinnamaldehyde, HCMO: dihydrocinnamyl alcohol.
α-Al₂O₃. Addition of bulky 4,7-diphenyl-1,10-phenanthroline significantly decreased the yield of the target compound, especially 9-phenylanthracene, which suggests that the coupling reaction for bulkier compounds like 9-phenylanthracene mainly occurred on Pd on the external surface of TPA-Cr.

In summary, using Pd(NH₃)₄(NO₃)₂ dissolved in water, fine Pd particles were formed in the micro- and meso-pores of TPA-Cr. In contrast, using PdCl₂ dissolved in water or methanol, Pd particles of a few to ca. 100 nm size were mainly formed on the external surface of TPA-Cr. Hydrogenation of cinnamaldehyde occurred in the micro- and meso-pores of TPA-Cr. Poisoning with bulky 4,7-diphenyl-1,10-phenanthroline drastically retarded the cross-coupling reaction on Pd/TPA-Cr, indicating that the cross-coupling reaction between 9-bromoanthracene and phenylboronic acid proceeded mainly on Pd on the external surface of TPA-Cr.

4. Regioselective Hydrogenation of *trans*-1-Phenyl-1,3-butadiene on Modified Pd/MOF Catalysts

Our previous findings indicated that the position of the precious metal in the micropores or on the exterior of MOF is important for reactions. Regioselective hydrogenation and chemoselective hydrogenation are important for the synthesis of intermediates for pharmaceutical chemicals and several studies have used MOFs as supports.

We investigated regioselective hydrogenation of diene, *trans*-1-phenyl-1,3-butadiene over Pd/TPA-Cr catalyst (Scheme 2). In particular, the effects of the core-shell structure and t-butoxycarbonyl modification (t-Boc modification) of MOF were studied in detail.

The core MIL-101 type MOF consisting of Cr³⁺ and nitroterephthalic acid was prepared according to reference methods. Core-shell type MOF was prepared with light yellow NO₂-MOF-Cr, Cr(NO₃)₃·9H₂O and terephthalic acid, and the same procedure was used for the synthesis of core-shell MOF to obtain NO₂-MOF-Cr@MOF-Cr. Reduction of the nitro group of NO₂-MOF-Cr@MOF-Cr was carried out with SnCl₂·2H₂O to obtain light green NH₂-MOF-Cr@MOF-Cr. Finally, Pd(NO₂-MOF-Cr@MOF-Cr was prepared using NH₂-MOF-Cr@MOF-Cr, PdCl₂ and HClaq. After filtration, washing and drying, the obtained catalyst precursor material was reduced at 200 °C under a hydrogen stream.

To narrow the micropores of the core NH₂-MOF-Cr, the amino group of core NH₂-MOF-Cr was modified.
with t-butoxycarbonyl (t-Boc modification) by mixing Pd/NH₂-MOF-Cr@MOF-Cr with di-t-butyl dicarbonate at room temperature to obtain Pd/(CH₃)₃COCONH-MOF-Cr@MOF-Cr. Hydrogenation of trans-1-phenyl-1,3-butadiene was carried out batchwise in an autoclave.

XRD patterns of NO₂-MOF-Cr, NO₂-MOF-Cr@MOF-Cr, 1 wt% Pd/NH₂-MOF-Cr@MOF-Cr and 1 wt% Pd/(CH₃)₃COCONH-MOF-Cr@MOF-Cr were substantially the same, and accorded with that of MOF-Cr, MIL-101[29]. No XRD peaks ascribed to Pd were observed for Pd-loaded catalysts, suggesting that Pd was highly dispersed in the micropores of MOF. Slight decreases in BET surface areas were found for 1 wt% Pd/NH₂-MOF-Cr@MOF-Cr and 1 wt% Pd/(CH₃)₃COCONH-MOF-Cr@MOF-Cr compared to the starting material NO₂-MOF-Cr@MOF-Cr. FT-IR spectra for catalysts with t-Boc modification showed peaks ascribed to CH₃, C=O and C-N vibrations, suggesting that the amino group of NH₂-MOF-Cr was modified as expected.

Figure 2 shows the X-ray photoelectron spectroscopy (XPS) spectra for N1s for NH₂-MOF-Cr@MOF-Cr without and with Ar etching, which suggests that the core NH₂-MOF-Cr was covered with shell MOF-Cr. One interesting effect of the amino group on loading of Pd was observed (Table 5). Pd was not supported on MOF-Cr, whereas Pd species interacted with the amino group and was rapidly loaded for NH₂-MOF-Cr@MOF-Cr. This suggests that Pd is located near the amino group with high dispersion and also Pd that is located only in the micropores of core NH₂-MOF-Cr. Consequently, we can anticipate the confined effect within the microporous structure of MOF.

The results for regioselective hydrogenation of trans-1-phenyl-1,3-butadiene are given in Table 6. Under the conditions adopted, conversion of trans-1-phenyl-1,3-butadiene was 100% for every catalyst, suggesting that the substrate quickly diffused in the micropores of MOF-Cr. Without MOF shell (Entry 1), 1-phenyl-3-butene ((b) in Scheme 2) was obtained. Without t-Boc modification (Entry 2) and with a small amount of shell (Entry 3), (b) was the major product even with t-Boc modification. Interestingly, with the optimum amount of shell and t-Boc modification (Entries 4, 5), trans-1-phenyl-1-butene ((c) in Scheme 2) was obtained with 60 to 70% selectivity. Shell formation carried out with larger amounts of Cr(NO₃)₃·9H₂O and terephthalic acid (Entry 6) resulted in low selectivity for (c), probably because MOF-Cr was formed independent of the seed NO₂-MOF-Cr. These results indicate that with location of all Pd in the micropores of MOF and with sufficient structural strain induced in the MOF, for example by t-Boc modification, regioselective hydrogenation of the end C=C double bond is possible.

| Entry | Support | Shell preparation | Conv. (%) | Selectivity (%) |
|-------|---------|-------------------|-----------|-----------------|
|       |         | Cr(NO₃)₃·9H₂O [g] |           | (b) (c) (d)    |
| 1     | (CH₃)₃COCONH-MOF-Cr | – | 100 | 82.5 15.2 2.3 |
| 2     | NH₂-MOF-Cr@MOF-Cr | 1.34/0.88 | 100 | 97.2 1.1 1.7 |
| 3     | (CH₃)₃COCONH-MOF-Cr@MOF-Cr | 0.67/0.44 | 100 | 71.4 26.6 2.0 |
| 4     | (CH₃)₃COCONH-MOF-Cr@MOF-Cr | 0.67/0.44 + 0.67/0.44 | 100 | 35.3 60.7 4.0 |
| 5     | (CH₃)₃COCONH-MOF-Cr@MOF-Cr | 1.34/0.88 | 100 | 26.0 70.7 3.2 |
| 6     | (CH₃)₃COCONH-MOF-Cr@MOF-Cr | 3.35/2.20 | 100 | 97.9 0.0 2.1 |

a) Catalyst 10.0 mg (Pd loading 1 wt%), trans-1-phenyl-1,3-butadiene 1.54 mmol, Triglyme 10.0 g, Temp. 65 °C, 3 h, P₈2: 5.0 MPa.

b) (b): 1-Phenyl-3-butene, (c): trans-1-Phenyl-1-butene, (d): 1-Phenylbutane.

Fig. 2 N1s XPS Profiles of NH₂-MOF-Cr@MOF-Cr
5. Kinetic Separation of Alkylbenzenes with MOFs

The unique properties of MOFs have various potential applications such as adsorbent, catalyst and so on. MOFs have been tested for separation of aromatics and aliphatic hydrocarbons. We evaluated MOFs with pore sizes smaller than 1 nm for chromatographic separation of alkylbenzenes to investigate the separation mechanism.

Five MOFs, TPA-Cr, TPA-In, TPA-Cu, TPA-Al and TPA-Zn, were prepared for the chromatographic separation of alkylbenzenes. MOF was pulverized and sieved under 100 mesh, and placed in a Pyrex glass column with both ends filled with quartz glass wool plugs. The front end was connected to the heated injection port and the other end was connected to the thermal conductivity detector of a gas chromatograph. MOF was pre-treated in-situ at 200 °C for 1 h before injection of the probe molecule, and then various probe molecules 0.20 μL were pulsed with a microsyringe. Column temperature was varied between 150 °C and 220 °C. Retention (elution) time (peak top time) was used for the following analyses.

MOFs were thermally stable at 300 °C or higher temperatures except TPA-Cu (ca. 270 °C). Field emission-scanning electron microscope (FE-SEM) images for the five MOFs indicated that the morphologies of TPA-Cr, TPA-Al and TPA-Zn were very similar, consisting of aggregates of 30 to 100 nm particles. On the other hand, the morphologies of TPA-In and TPA-Cu were different. FE-SEM images suggested the amounts of impurities were very small in the five MOF materials.

Typical results for the elution behaviors are shown in Fig. 4 for TPA-Al (trivalent cation, 0.6 nm) and TPA-Cr (trivalent cation, 0.9 nm). The retention time of each molecule was longer for TPA-Al (0.6 nm) than for TPA-Cr (0.9 nm). Table 7 shows the retention times for the probe molecules for various MOFs. Order of retention time differed in some MOFs, and probably due to the interaction between the MOFs and probe molecules.

The dependence of retention time on temperature for benzene is shown for TPA-Cu in Fig. 5. Here, the retention time was positively correlated with the diffusion rate; so a high diffusion rate resulted in a short retention time. Thus, if retention is based on diffusion, the diffusivity coefficient related to the retention time depends on the temperature as follows: \( D_T = D_0 \exp(-Ea/RT) \), where \( D_T \) is the diffusivity coefficient \((D)\) at absolute temperature \( T \), \( D_0 \) is \( D \) at a defined temperature, \( Ea \) is the activation energy for diffusion, and \( R \) is the gas constant. Plots for \( 1/T \) versus \( \ln(1/(\text{retention time})) \) are given in Fig. 6. The apparent activation energy \( Ea \) (kJ mol\(^{-1}\)) for diffusion was calculated from the slope (Table 8). \( Ea \) for benzene was about 50 kJ mol\(^{-1}\) for the three small pore MOFs, TPA-Zn, -Cu and -Al, whereas \( Ea \) for TPA-Cr was 38 kJ mol\(^{-1}\). Interestingly, \( Ea \) for benzene was far smaller, 26 kJ mol\(^{-1}\) for TPA-In. If molecular diffusion governs retention, the \( Ea \) for each MOF should be similar. Furthermore, the order of magnitude of \( Ea \) was not correlated with that of the pore sizes of MOFs. If diffusion is controlled...
only by the pore size, the retention times for TPA-Cr should be shorter than that for TPA-In. Therefore, the interactions between the MOFs and probe molecules may have controlled the diffusion and are important for $E_a$.

In summary, investigation of the chromatographic elution behaviors of various alkylbenzenes revealed that the main cause of separation was diffusion controlled by the interaction between the probe molecules and MOF surfaces.

**Table 7**  
Retention Times for Various Probe Molecules with MOFs

| MOF   | Pore size [nm] | Benzene | Toluene | EB   | Styrene | 2-MS | Retention time [min] |
|-------|----------------|---------|---------|------|---------|------|---------------------|
| TPA-Cu| 0.6            | 1.42    | 2.59    | 4.38 | 6.87    | 7.12 |                     |
| TPA-In| 0.6            | 0.83    | 2.08    | 4.98 | 5.79    | 18.6 |                     |
| TPA-In| 0.6            | 4.46    | 5.85    | -    | -       | -    |                     |
| TPA-In| 0.7            | 0.84    | 1.16    | 1.68 | 2.06    | 2.98 |                     |
| TPA-Cr| 0.9            | 1.00    | 1.92    | 3.29 | 4.21    | -    |                     |

EB: ethylbenzene, 2-MS: 2-methylstyrene.
Sample: 0.2 μL, Column temp.: 200 °C, Injection/Detector temp.: 240 °C, N₂ 85 mL min⁻¹ (STP).

**Fig. 4** Chromatograms for Various Alkylbenzenes Separated Using TPA-Cr and TPA-Al

**Fig. 5** Effect of Column Temperature on Retention Time of Benzene with TPA-Cu

**Fig. 6** Arrhenius-type Plot for Benzene with TPA-Cu
6. Molecular-sieving Separation of \( p \)-Xylene with MOFs

\( p \)-Xylene is an important raw material for terephthalic acid and the co-monomer for polyethylene terephthalate. Presently, \( p \)-xylene is produced by separation from mixed xylenes by adsorption with zeolite or crystallization. These conventional methods have some drawbacks and are costly. Therefore, a new process to separate \( p \)-xylene at lower cost is desirable.

MOFs have been investigated for the separation of xylenes. In most cases, xylenes were diffused into micropores and separation was governed by the diffusion rate based on the molecular size of the xylenes and/or by the interaction between the MOF surface and diffusing molecules.

Here, a number of microporous MOFs were prepared for vapor-phase chromatographic separation of \( p \)-xylene from mixed xylenes and ethylbenzene, especially to investigate the potential for molecular sieving.

Fourteen types of MOFs were prepared according to the literature procedures as shown in Table 8. The setup for the separation experiments is the same for section 5. After in-situ pre-treatment at 200 °C for 1 h, a probe molecule or a mixture of xylenes was injected as a pulse of 0.20 to 2.0 \( \mu \)L. Column temperature was varied between 100 °C and 220 °C. Elution time (peak top time) was used for the following analyses.

Table 10 summarizes the properties of the MOFs and the results for separation of xylenes and ethylbenzene (EB). Most MOFs were well crystallized except fumaric acid (FMA)-Ti, FMA-Fe and TPA-Zn. The MOFs were prepared according to the reported methods, but some MOFs were difficult to prepare with high crystallinity and purity.

Separation properties could be categorized into three types. In Category 1, xylenes and EB were eluted at the same elution time of ca. 0.2 min. A representative chromatographic image is given in Fig. 7a). In Category 1, xylenes and EB passed through the spaces between MOF particles. In Category 3, the elution times for xylenes and EB were longer and varied among the MOFs. A representative chromatographic image is given in Fig. 7b). The diffusion rate of \( p \)-xylene with the smallest kinetic diameter was higher in the micropores in most of these MOFs. As the order of elution was different among the MOFs, both the size of the micropores and the interactions between the MOF and the xylenes and EB may have affected the diffusion times.

In Category 2, \( o \)- and \( m \)-xylenes eluted quickly at ca. 0.2 min and a small peak for \( p \)-xylene appeared thereafter (Fig. 7c). This different elution behavior from Categories 1 and 3 suggests that \( p \)-xylene passed through the micropores of the MOF whereas \( o \)- and \( m \)-xylenes with larger kinetic diameters passed through the spaces between the MOF particles. These findings for Category 2 suggest that xylenes could be separated by the molecular-sieving mechanism.

The xylene mixture (\( ortho : meta : para = 1 : 1 : 1 \) molar ratio) was separated into one immediate peak of \( o \)- and \( m \)-xylene and one later peak of \( p \)-xylene. Increase of the column temperature from 170 to 200 °C at 2 min after the injection caused \( p \)-xylene to be eluted with ca. 77 % purity. Industrial separation currently uses X-type zeolite as the adsorbent, so all xylenes pass through the zeolite micropores, suggesting the necessity of a large micropore volume to accommodate all the xylenes. On the other hand, only \( p \)-xylene diffuses into the micropores of the FMA-Zr MOF, so the necessary amount of MOF is smaller than that of zeolite. This is beneficial because the separator can be smaller, which reduces the investment and separation costs.

Up to now, the separation was carried out in the
vapor phase, whereas separation in the liquid phase will not require energy for the vaporization of xylenes. Therefore, three xylene isomers, 0.25 mL each, were dissolved in 1,3,5-trimethylbenzene and FMA-Zr was added at room temperature. Small and similar adsorption of each xylene was observed, probably because the xylenes were adsorbed on the outer surface of FMA-Zr. Therefore, the temperature for separation is important and the pore mouth is wider at higher temperatures to allow p-xylene to diffuse into the micropores. Consequently, the separation temperature was carefully investigated.

The temperature adopted in the vapor phase separation was 170 °C (Fig. 7c), at which o- and m-xylene eluted quickly at the same elution time and the peak for p-xylene was very small. At 100 °C (Fig. 8a), all three xylenes eluted almost at the same elution time. At 200 °C (Fig. 8c), the peak for m-xylene at ca. 0.2 min became smaller, which suggests that the pore mouths became wider due to thermal vibration of the MOF structure to allow diffusion of m-xylene into the micropores. At 140 °C (Fig. 8b), a similar separation pattern to that at 170 °C (Fig. 7c) was observed. As the pore mouth of FMA-Zr would be smaller at 170 °C, higher purity of p-xylene would be expected. MOF structure change occurs with higher temperatures, but the present results are the first one to utilize this effect for separation.

Stability of FMA-Zr was studied by repeating pulses at 170 °C and by heating FMA-Zr at 200 °C to elute the adsorbed p-xylene, showing that FMA-Zr (MOF-801) was robust for repeated adsorption of xylene and heat treatment at 200 °C.

In summary, various MOFs were prepared and used...
for the separation of \( p \)-xylene from mixed xylenes. MOFs with a critical pore mouth size could separate \( p \)-xylene from \( o \)- and \( m \)-xylenes by the molecular-sieving mechanism. The temperature for separation was very important for the molecular sieving process. Furthermore, FMA-Zr, MOF-801, consisting of fumaric acid and Zr\(^{4+}\) was robust for this separation.

7. Summary

MOF is a useful material as a catalyst support and for molecular-sieving separation. To utilize MOF effectively, the relationship between the size of the micropores and the substances to react or separate is decisively important. Furthermore, for the practical application of MOFs, comparison with conventional catalysts and separation methods needs to assess catalytic performance, energy input and cost of MOF, and the process to be achieved.

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要  旨
石油化学関連プロセスへの応用におけるMOFの結晶性とミクロ細孔性構造の重要性
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金属有機構造体（MOF）は、ミクロ細孔、結晶構造そして高い比表面積と言った特徴を有している。これらの特性は、吸着／分離、触媒担体／触媒、その他のプロセスにおいて利点となる。本レビューは、MOFの解説、キャラクタリゼーション

MOF の有用性を示すため、エチレンのオリゴマー化、シナ

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