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Effect of pore sizes on catalytic activities of arenetricarbonyl metal complexes constructed within Zr-based MOFs[†]

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Arenetricarbonyl metal complexes ([$-phM(CO)_3-$] and [$-biphM(CO)_3-$]; ph = phenylene, biph = biphenylene, M = Mo, Cr) constructed within Zr-based MOFs act as highly active and selective catalysts for epoxidation of cyclooctene. Catalytic activities of these complexes are enhanced with increasing the pore sizes of Zr-based MOFs.

There has been intensive interest in the immobilization of guest molecules onto solid surfaces in the light of the unique and efficient material design which enables the integration of chemical properties controlled at the molecular level and the rigidity of solid supports. Heretofore, various combinations of guest molecules and solid supports have been attempted for applications to catalysts, luminescence materials, sensors and so on.¹⁻⁶ Among those, in the field of catalysts, organometallic complex molecules have attracted the interest of researchers, because they often exhibit excellent catalytic activity and selectivity. Moreover, their catalytic reactivity is readily tuned by varying their ligands.^{7,8} In addition, the immobilization of organometallic complex molecules onto solid supports allows for the transformation of processes from homogeneous to heterogeneous. The utilization of the heterogeneous catalytic system will enable one to reuse the catalysts and to avoid time consuming and extra purification processes caused by the use of homogeneous catalysts.

On the other hand, since the characteristics of organometallic complexes as guest molecules are influenced strongly by steric and electrostatic constraints derived from solid supports, the design of an appropriate reaction field by the selection of

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solid supports is of significant importance.9,10 Metal-organic frameworks (MOFs), also called porous coordination polymers (PCPs), are promising candidate materials for solid supports owing to their extremely high specific surface areas and large pore volumes.^{11,12} Among these MOFs, Zr-based MOFs are particularly interesting materials due to high chemical and thermal stability.^{13–15} In addition to these unique features, the structures and chemical properties of MOFs can be varied by changing the combination of organic linkers and metal nodes constituting their microporous frameworks. So far, for example, unique adsorbents and acid or base catalysts have been developed by using organic linkers bearing various substituent groups.^{2,11,12,16-18} Moreover, Kaye et al. and Chavan et al. have reported the construction of organochromium complexes within the frameworks of MOFs by using a ligand exchange reaction between chromium hexacarbonyl $(Cr(CO)_6)$ and benzene rings belonging to organic linkers of MOFs.^{14,18} In these complexes, chromium centers are directly coordinated to benzene rings within the frameworks of MOFs. Such organometallic complexes constructed within MOF frameworks are expected to exhibit high catalytic performances owing to their closely similar coordination environments to molecular ones. Furthermore, accurate design of reaction fields based on the structure diversity of MOFs makes it possible to develop unique and efficient heterogeneous organometallic complexes catalysts.

In the present study, arenetricarbonyl complexes ([-phM- $(CO)_3$ -] and [-biphM $(CO)_3$ -]; ph = phenylene, biph = biphenylene, M = Mo, Cr) have been constructed within Zr-based MOFs with different pore sizes and their heterogeneous catalytic activities have been evaluated. The detailed characterization of local structures of these arenetricarbonyl complexes and the effects of pore size on their catalytic activities are described and discussed below.

Zr-based MOFs named UiO-66 and UiO-67 were prepared by a conventional solvothermal method using 1,4-benzenedicarboxylic acid and 4,4'-biphenyldicarboxylic acid (BPDC) as organic linkers, respectively.¹⁵ [$-phM(CO)_3-$] and [$-biphM(CO)_3-$] complexes were then constructed within UiO-66 and

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UiO-67, respectively, by a chemical vapor deposition (CVD) technique (Scheme 1).^{19–21} Specifically, in the synthesis of Mo complexes, UiO-66 or UiO-67 degassed at 473 K for 1 h to remove the adsorbed water molecules on the surface was subjected to $Mo(CO)_6$ vapor at 373 K for 3 h *in vacuo*. After that, unreacted and physisorbed $Mo(CO)_6$ was removed by evacuation at 423 K for 1 h, yielding UiO-66-Mo(CO)₃ or UiO-67-Mo(CO)₃. The [-phCr(CO)₃-] and [-biphCr(CO)₃-] complexes constructed within UiO-66 and UiO-67 (UiO-66-Cr(CO)₃ and UiO-67-Cr(CO)₃, respectively) were prepared by the same method except that the CVD treatment was performed at 393 K using Cr(CO)₆ as a starting material.

Fig. 1 shows XRD patterns of UiO-66 and UiO-67 before and after CVD treatments for the construction of arenetricarbonyl complexes. The diffraction patterns of UiO-66 and UiO-67 before CVD treatment were in good agreement with previous reports, indicating that MOF framework structures having micropores were successfully formed.^{15,22,23} It should be noted that the position of the diffraction peak at the lowest angle in the pattern of UiO-67 ($2\theta = 6^{\circ}$), which is associated with the pore size, was lower than that of UiO-66 ($2\theta = 8^{\circ}$). This finding shows that the longer organic linker, BPDC, leads to the expansion of the pore size of UiO-67 as compared to UiO-66. After CVD treatment, the diffraction patterns of UiO-66 and UiO-67 were nearly unchanged regardless of the kind of starting materials (*i.e.*, Cr(CO₆) or Mo(CO)₆), suggesting that the CVD



Fig. 1 XRD patterns of (a) UiO-66, (b) UiO-66-Mo(CO)₃, (c) UiO-66-Cr(CO)₃, (d) UiO-67, (e) UiO-67-Mo(CO)₃ and (f) UiO-67-Cr(CO)₃.



Fig. 2 FT-IR spectra of (A) UiO-66-Mo(CO)₃ and (B) UiO-67-Mo (CO)₃ recorded after evacuation at (a, c) 473 K and (b, d) 523 K for 1 h.

treatment for the immobilization of metal complexes onto UiO-66 and UiO-67 did not influence their framework structures.

Subsequently, FT-IR measurements were performed to confirm the formation of arenetricarbonyl complexes within MOF frameworks. FT-IR spectra were collected after evacuation at 473 K or 523 K for 1 h. Fig. 2 shows FT-IR spectra of UiO-66-Mo(CO)₃ and UiO-67-Mo(CO)₃ evacuated at 473 K and 523 K. UiO-66 and UiO-67 before CVD treatments exhibited no peaks in the measurement range (data not shown). After CVD treatments, observable peaks were seen in spectra of UiO-66-Mo-(CO)₃ and UiO-67-Mo(CO)₃ evacuated at 473 K around 1990-1980 cm⁻¹ and 1940-1910 cm⁻¹. In general, the molecular C₆H₆Mo(CO)₃ complex shows two kinds of IR-active CO vibrational peaks at 1987 and 1916 cm⁻¹ assignable to ν (CO)_{a1} and $\nu(CO)_e$ vibrational modes, respectively.²⁴ By contrast, the IR spectrum of Mo(CO)₆ has mainly one strong IR-active CO vibrational peak at 1985 cm⁻¹ assignable to the $\nu(CO)_{Eg}$ vibrational mode.²⁴ These results and information suggest that the molybdenum center is directly coordinated to phenylene and biphenylene rings belonging to organic linkers of MOFs through the CVD treatment to form [-phMo(CO)₃-] and [-biphMo(CO)₃-] complexes within MOFs. Furthermore, these CO vibrational peaks of [-biphMo(CO)₃-] complexes were shifted to lower wavenumbers than [-phMo(CO)₃-] complexes. These peak shifts were attributed to high electron-donating power of biphenylene moieties of UiO-67.25 These CO

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vibrational peaks completely disappeared after evacuation at 523 K for 1 h. This finding indicates that the arenetricarbonyl complexes were decomposed by heat treatments. Similar results were obtained in FT-IR spectra of UiO-66-Cr(CO)₃ and UiO-67-Cr(CO)₃; [-phCr(CO)₃-] and [-biphCr(CO)₃-] complexes were confirmed to be constructed within MOFs (Fig. S1[†]).

Molybdenum tricarbonyl complexes are known to be effective catalysts for epoxidation of olefins with tert-butyl hydroperoxide (TBHP) as an oxidant. In these reactions, molybdenum tricarbonyl complexes undergo oxidative decarbonylation with TBHP to form oxomolybdenum(vi) species, such as Cp'MoO₂X and/or Cp'MoO(O₂)X.^{1,26,27} These oxomolybdenum (vi) species act as highly active catalytic sites for the epoxidation reaction with TBHP as an oxidant. Based on the successful formation of arenetricarbonyl complexes within MOFs, epoxidation of cyclooctene with TBHP over UiO-66-M(CO)₃ and UiO-67-M(CO)₃ was attempted under an N_2 atmosphere (Scheme 2). As shown in Table 1, UiO-66-Mo(CO)₃ and UiO-67-Mo(CO)₃ promoted the epoxidation reaction and gave cyclooctene oxide with almost 100% selectivity. In contrast, the epoxidation reaction hardly proceeded over UiO-66 and UiO-67 without [-phM(CO)₃-] and [-biphM(CO)₃-] complexes, respectively. These results indicate that arenetricarbonyl complexes constructed within MOFs are necessary to continue the reaction. Although UiO-66-Cr(CO)₃ and UiO-67-Cr(CO)₃ showed catalytic activities for the epoxidation reaction (Fig. S2⁺), their catalytic activities were lower than those of UiO-66-Mo(CO)₃ and UiO-67-Mo(CO)₃. It is noteworthy that UiO-67-M(CO)₃ showed higher activity than UiO-66-M(CO)₃. These catalytic enhancements would be due to the difference in the facility of substance diffusion between UiO-67 and UiO-66. Although both porous structures consist of an array of tetrahedral and octahedral cavities, the longer organic linker, BPDC, leads to the expansion of pores of UiO-67 compared with UiO-66. The diameters of tetrahedral and octahedral micropores in UiO-67 (12 and 16 Å, respectively) are larger than those in UiO-66 (7.5



Table 1 Epoxidation of cyclooctene on various catalysts at 328 K

Catalyst	Reaction time (min)	Conv. (%)	Sel. ^a (%)
UiO-66	15	Trace	_
UiO-67	15	Trace	_
UiO-66-Mo(CO) ₃	15	68	>99
UiO-67-Mo(CO) ₃	15	92	>99
UiO-66-Cr(CO) ₃	180	29	>99
UiO-67-Cr(CO) ₃	180	43	>99
UiO-67-Mo(CO) ₃	180	100	>99
UiO-67-Mo(CO) ₃ 2nd run	180	100	>99
UiO-66-Mo(CO) ₃ 3rd run	180	97	>99

^a Selectivity to cyclooctene oxide.

and 12 Å, respectively).²³ Since the tetrahedral pore size of UiO-66 (7.5 Å) is smaller than the molecular size of cyclooctene (*ca.* 8 Å), substance diffusion is considered to influence their catalytic activities strongly. These data indicate that the accessibility of cyclooctene to catalytically active sites is partially-hindered by smaller pores in UiO-66. Hence, the catalytic activity of UiO-67-Mo(CO)₃ was higher than that of UiO-66-Mo-(CO)₃. In these reactions, oxomolybdenum(vı) species formed during the reaction would promote the epoxidation of cyclooctene as follows: the formed complexes coordinate with TBHP at the molybdenum center and react with cyclooctene to produce cyclooctene oxide and *tert*-BuOH as a by-product.^{28,29} In fact, an amount of *tert*-BuOH equivalent to that of the cyclooctene to support the reaction mechanism.

On the other hand, epoxide groups are known to react with water and alcohol to yield diol and ether, respectively, in the presence of a Lewis acid.³⁰ Considering the fact that Zr clusters within UiO-67 act as Lewis acid catalysts and that the reaction mixture contains water derived from commercially available TBHP and *tert*-BuOH as the by-product, the produced epoxide seems to react with them when the reaction time is prolonged.⁶ In order to investigate the influence of reaction time on epoxide selectivity, the epoxidation reaction was carried out over UiO-67-Mo(CO)₃ upon prolonged reaction time (from 15 min to 180 min). The conversion of cyclooctene reached almost 100% after 3 h. It should be noted that the selectivity of cyclooctene oxide remained nearly unchanged, even on prolonging the reaction time. This result reveals that Zr clusters within UiO-67-Mo(CO)₃ did not act as a Lewis acid under these reaction conditions, revealing that UiO-67-Mo(CO)₃ showed excellent selectivity. In addition, from the results of a leaching test (Fig. S3[†]), we confirmed that the oxidation reaction proceeds just slightly after the catalyst was filtered off at the reaction temperature. This result indicates that the majority of the catalytically active oxomolybdenum species in UiO-67 are stably present in UiO-67 during epoxidation reaction. Furthermore, XRD patterns of UiO-67-Mo(CO)₃ before and after the epoxidation reaction show that the crystal structure of UiO-67-Mo(CO)₃ is almost maintained after epoxidation reaction (Fig. S4⁺). Finally, the reusability of UiO-67-Mo(CO)₃ was investigated. After the reaction, the solid catalyst was collected by filtration, washed several times with *n*-hexane, dried at room temperature and reused in the next catalytic cycle. The recovered catalyst was found to be recycled without significant loss of its catalytic activity for at least 3 cycles, suggesting that the catalytically active oxomolybdenum species are stably present in UiO-67 and act as a reusable heterogeneous catalyst.

In summary, $[-phM(CO)_3-]$ and $[-biphM(CO)_3-]$ complexes were successfully constructed within UiO-66 and UiO-67, respectively, by a CVD treatment using $M(CO)_6$. The metal centers of these complexes were directly coordinated to phenylene and biphenylene rings belonging to organic linkers of MOFs. UiO-66- $M(CO)_3$ and UiO-67- $M(CO)_3$ exhibited high catalytic activities and selectivities for epoxidation of cyclooctene with TBHP. Moreover, UiO-66- $Mo(CO)_3$ and UiO-67- $Mo(CO)_3$ **Dalton Transactions**

showed higher catalytic activity than UiO-66-Cr(CO)₃ and UiO-67-Cr(CO)₃. It is noteworthy that UiO-67-M(CO)₃ exhibited higher activity than UiO-66-M(CO)₃ due to the high accessibility of substrates to catalytically active sites attributable to large pores of UiO-67. The recovered UiO-67-Mo(CO)₃ was found to be recycled without significant loss of its catalytic activity, suggesting that the catalytically active oxomolybdenum species are stably present in UiO-67 and act as a reusable heterogeneous catalyst.

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