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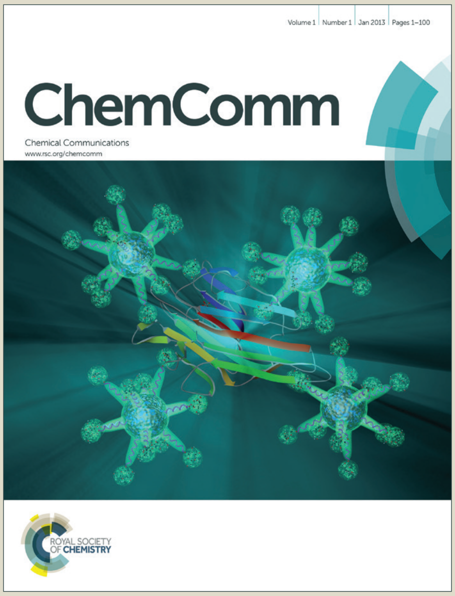

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

View Article Online
DOI: 10.1039/C4CC07562E

ARTICLE TYPE

Dependence of Crystal Size on the Catalytic Performance of a Porous Coordination Polymer

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Submicrosized MOF-76(Yb) exhibits higher catalytic performance for esterification than microsized MOF-76(Yb). Control of the crystal size of porous heterogeneous catalysts, such as PCP/MOFs, offers a promising approach to fabricating high-performance catalysts based on accessibility to the internal catalytic sites.

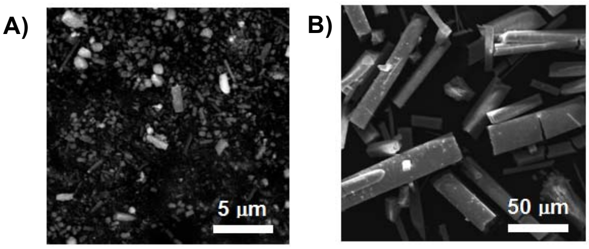

Fig. 1. SEM images of (A) **1a** and (B) **1b**.

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) are receiving considerable attention for their potential application in gas storage, molecular separation, heterogeneous catalysts, and catalyst supports.[1–4] PCP/MOFs as heterogeneous catalysts offer the advantage of having a high surface area together with a large number of potentially active sites.[5–11] Another important aspect is their potential to act as molecular sieves and to select the size and polarity of the molecules that can diffuse inside the channels to undergo reactions.[7,12] While internal diffusion limitations in microporous materials can be used positively to select and react a given substrate present in a mixture, there are other occasions where severe restrictions on substrate diffusion within the channels result in a low turnover frequency (TOF) because only the active sites at the external surface or internal pores close to the crystal surface are accessible to substrates.[13] Here, we report on the synthesis of two types of MOF-76(Yb) (molecular formula = $[YbBTC]_\infty$) with one-dimensional (1-D) channels[14] and crystals with markedly different sizes: one was 50 µm (micrometer sized, > 1 µm) and the other was 0.8 µm (submicrometer sized, 100 nm–1 µm). We demonstrated that submicrosized MOF-76(Yb) could show a higher catalytic performance than microsized MOF-76(Yb) because the high diffusion of the substrates into internal pore surface leads to the large number of practically functionalizing catalytic sites.

Submicrosized MOF-76(Yb)$\cdot(H_2O)\cdot(DMF)_{1.1}$ (denoted as **1a**$\supset$solv) was successfully synthesized at room temperature (for details, see ESI†). The **1a**$\supset$solv were activated in vacuum at 300 °C for 1 h to generate the open metal site (OMS), which functionalizes as a catalytic site, located in the corner of **1a**. The microsized MOF-76(Yb)$\cdot(H_2O)\cdot(DMF)_{1.1}$ (denoted as **1b**$\supset$solv) was also synthesized using a solvothermal synthesis route.[15] The difference between the crystal size of **1a** and **1b** was confirmed using SEM (Fig. 1). Both compounds comprised particles with column-like structures having high aspect ratios. However, particles of **1a** (length = ca. 0.8 µm, width = 0.4 µm) were significantly smaller than particles of **1b** (length = ca. 50 µm, width = 10 µm). This difference in crystal size resulted in a greater external surface area and an internal pore surface close to the external surface in **1a**. The crystals of **1a** and **1b** were compared regarding their structure, sorption properties, Lewis acidity of the Yb^{III}, and catalytic activity. The X-ray powder diffraction (XRPD) patterns of **1a** and **1b** were in good agreement with the simulated pattern of MOF-76(Yb) (Fig. S1, ESI†).[15] Both compounds exhibited Type I isotherms in N_2 sorption measurements at 77 K with no hysteresis. The Brunauer–Emmett–Teller surface area of **1a** was 706 m^2g^{-1} with a pore volume of 0.286 cm^3g^{-1}, whereas the corresponding values for **1b** were 702 m^2g^{-1} and 0.280 cm^3g^{-1}, respectively (Fig. S2, ESI†). The thermogravimetric analysis (TGA) profiles of **1a** and **1b** were identical (Fig. S3, ESI†). The acidity of **1a** and **1b** were evaluated using two methods. First, the acidity of the OMS of Yb^{III} was evaluated from the temperature-programmed desorption of ammonia (NH_3-TPD), which is commonly used to determine the acidity of zeolites.[16] As summarized in Table 1, both **1a** and **1b** showed a small desorption peak in the low-temperature region (165 °C). The observed acid density of Yb^{III} in **1a** (0.634 $mmolg^{-1}$) and **1b** (0.655 $mmolg^{-1}$) did not agree with the value calculated from their molecular formulas ($[YbBTC]_\infty$, 2.63 $mmolg^{-1}$).[15] These results indicate that the NH_3 was physically adsorbed on both **1a** and **1b**.[16] Next, the acidity of **1a** and **1b** were evaluated using an *in situ* spectroscopic method using acetone as a probe molecule.[17,18,20] When acetone is

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DOI: 10.1039/C4CC07562E

Table 1. Carbonyl-stretching vibration of acetone adsorbed on PCP/MOFs and the peak temperature of NH_3 desorption of the PCP/MOFs.

Porous materials	Acetone as probe		NH_3- TPD
	ν(C=O)/cm^{-1}	$\Delta\nu$(C=O)^{a}/cm^{-1}	T_{des}^{b}/ °C
1a (MOF-76(Yb))	1697.4	17.6	165 ^{c}
1b (MOF-76(Yb))	1697.4	17.6	165 ^{c}
La-BTTc	1686.0, 1698.0 ^{d}	29.0, 17.0 ^{d}	480, 500, (550) ^{d}
MIL-101(Cr)	1709.6 ^{d}	5.4 ^{d}	260 ^{e}
ZIF-8	1714.9 ^{d}	0.1 ^{d}	– ^{f}

^{a}Calculated by subtracting the observed value from the value for acetone (1715 cm^{-1}). ^{b}Peak temperature of NH_3 desorption. Smaller additional peaks are shown in parentheses. ^{c}Physical adsorption. ^{d}Ref. 17. ^{e}Ref. 19. ^{f}Not reported.

physically adsorbed on an acidic site, the C=O bond interacts with the acidic site, and this leads to a low-frequency shift of the peak assigned to $\nu_{C=O}$ (1715 cm^{-1} for gaseous acetone) in the infrared (IR) spectrum, and so the degree of acidity can be evaluated. Our results are summarized in Table 1 (for details, see ESI†). As expected, ZIF-8 with no acidic sites did not show an effect on the ν(C=O) stretch of the adsorbed acetone molecules compared with acetone itself. In contrast, PCPs with OMS, such as La-BTTc and MIL-101(Cr), showed a shift in the ν(C=O) stretch of acetone to a lower frequency. Among the PCPs tested, both **1a** and **1b** showed the same low-frequency shift (ca. 17.6 cm^{-1}), indicating an identical degree of acidity. Thus, the *in situ* spectroscopic method allowed us to evaluate the acidity, even when the probe molecule was not chemically adsorbed onto the acid sites. These results show that **1a** and **1b** have the same structure, porosity, and acidity, whereas other size-controlled synthesis methods lead to defective crystals.[21]

The isomerization reaction of 1-hexene was conducted as a model reaction to elucidate the difference in catalytic properties of **1a** and **1b** (Fig. 2B), because **1a** and **1b** show a resistance to heat (Fig. S3) and the Yb^{III}-modified porous material efficiently catalyzes this isomerization reaction.[22] A gradual increase in concentration of C_6 isomers was observed without any dependence on crystal size, together with some trace of products resulting from cracking and coupling reactions (for details, see ESI†). The non-dependence of the yields on the crystal size indicates that the 1-hexene could efficiently access the entire internal pore surfaces of both **1a** and **1b**. The microwave-assisted esterification reaction[23] of acetic acid with methanol was also examined to evaluate the catalytic performance of **1a** and **1b** under relatively mild conditions. Microwaves were used to raise the solution temperature for a period of 30 s, and the resulting solution temperature (100 °C) was maintained during the reaction. Both **1a** and **1b** catalyzed the esterification reaction of acetic acid with methanol, whereas a control experiment without any MOF-76(Yb) catalyst gave a low yield. Most significantly, the yield for **1a** was three times as large as that of **1b** (Fig. 2C). A filtering test was carried out to determine whether the reaction mechanism was heterogeneous or homogeneous. All the solution was separated from the reaction system using filtration for **1a** after 15 min (19% yield). Then, the filtrate was heated using microwaves (Fig. 2C(d)), and the reaction did not proceed further in the filtrate. Thus, this catalytic performance originates from the presence of the solid catalyst and is not caused by a molecular species contained in the solution. The filtering experiment made it clear that the mechanism was not homogeneous, but rather was heterogeneous. The benzoic acid was also examined as the substrate for the esterification reaction. This substrate is not able to enter into the pores (Fig. S8) and enough to undergo an esterification reaction with conventional Lewis acid catalysts.[24] Unlike the case of acetic acid, both **1a** and **1b** showed low catalytic activity not depending on the crystal size (Table S1, ESI†). This result indicates that there are no OMSs functionalizing as Lewis acid catalyst for the esterification reaction on the external surface. We can conclude that the Lewis acid-catalyzed esterification reaction is limited to the internal pore surfaces of **1a** and **1b**.

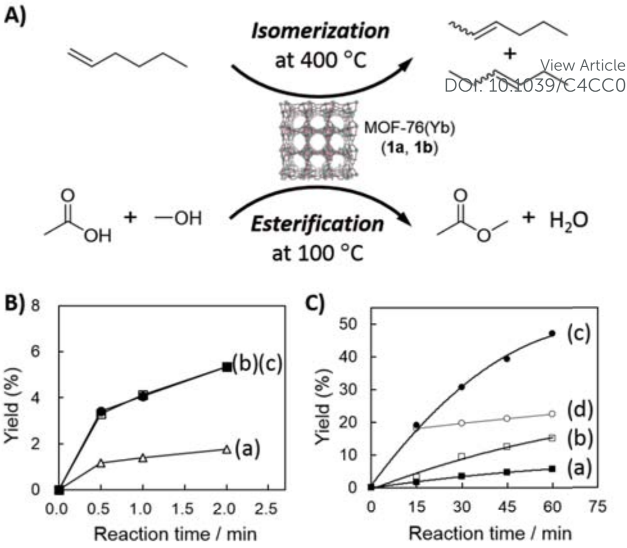

Fig. 2. (A) Reaction scheme of the isomerization reaction and the esterification reaction of MOF-76(Yb). (B) Isomerization reaction of 1-hexene at 400 °C. Yield of cis/trans-2-hexene and cis/trans-3-hexene (a) without catalyst, (b) on **1b**, and (c) on **1a**. (C) Microwave-assisted esterification reaction of acetic acid with

The dependence on the crystal size of the catalytic performance for several reactions was also investigated using UiO-66, MIL-101(Cr), and MOF-74(Co).[8–11] The TOFs are summarized in Fig. 3 (for details, see ESI†) to compare the catalytic performance of **1a** and **1b** with that of other PCP/MOFs. A non-dependence of the catalytic performance on the crystal size of UiO-66 and MIL-101(Cr) has been observed in the submicrometer region.[8–10] In addition, no dependency of the catalytic performance on the crystal size of MOF-74(Co) has been observed, whereas high pressure conditions lead to high TOFs.[11] These results show that there was no difference in substrate diffusion from using smaller sized particles, and that the size dependency differed from that of the metal nanoparticles in MIL-101.[25]

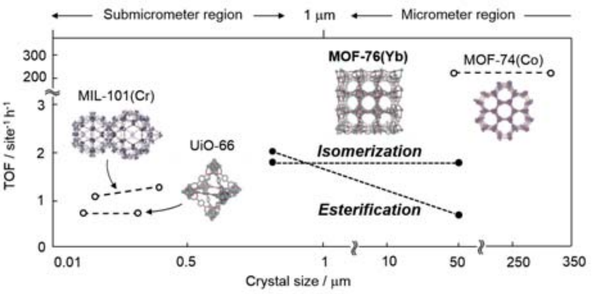

Fig. 3. Crystal size-dependence map for the four PCP/MOF catalysts discussed in this paper. The catalytic reaction is as follows: (MOF-76(Yb)), esterification reaction; (MOF-74(Co)), cycloaddition of CO_2 to styrene oxide[11]; (UiO-66), cyclization of (+)-citronellal[9]; and (MIL-101(Cr)), oxidation of diphenyl methane[8].

In contrast, the significant changes in size of the MOF-76(Yb) samples enhanced the catalytic performance during the esterification reaction, although **1a** and **1b** were identical in terms of their structure and acidity of the Yb^{III} cations, as evidenced by the XRPD, N_2 adsorption, and IR data using acetone as a probe molecule. A decrease in 1-D channel length would increase the number of OMSs functionalizing as catalytic sites inside the pores of the MOF-76(Yb). Quantitatively, the functionalizing OMS of **1a** was calculated to be about three times that of **1b** from the TOF for **1a** (2.6 h^{-1}) and **1b** (0.8 h^{-1}). This indicates that all the OMSs in the 1-D channels of **1a** are fully utilized as catalytic sites, whereas the number of practically functionalizing OMSs in **1b** is reduced by about one-sixth from the aperture window of the 1-D channels. On the other hand, in the case of the isomerization reaction, the significantly enhanced diffusion on the substrate driven by the high-temperature condition presumably leads to the non-dependence on the crystal size. From these results, we can conclude that heterogeneous PCP/MOF catalysts in the submicrometer region can offer better catalytic performance than in the micrometer region, but this depends on the diffusion rate of the substrate and the products of the target reaction.

In conclusion, submicrosized MOF-76(Yb) (**1a**) was prepared at room temperature. The structure and acidity of **1a** were found to be identical to those of microsized MOF-76(Yb) (**1b**). Compound **1a** exhibits higher catalytic performance for esterification than **1b**, whereas there was no difference between these compounds for the isomerization reaction studied. Thus, control of the crystal size of heterogeneous porous catalysts, such as PCP/MOFs, offers a promising approach to high-performance catalysts based on the large number of practically functionalizing OMSs.

This research was supported by the New Energy and Industrial Technology Development Organization, Japan (NEDO), the PRESTO Program of the Japan Science and Technology Agency (JST), the Advanced Catalytic Transformation Program for Carbon Utilization (ACT-C), the MEXT Project for Developing Innovation Systems Regional Innovation Strategy Support Program Kyoto Next-Generation Energy System Creation Strategy (MEXT = the Ministry of Education, Culture, Sports, Science and Technology of Japan). The Institute for Integrated Cell-Material Sciences (iCeMS) is supported by the World Premier International Research Initiative (WPI).

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization. See DOI: 10.1039/b000000x/

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