Site-Selective Catalysis of a Multifunctional Linear Molecule: The Steric Hindrance of Metal–Organic Framework Channels

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Owing to the complexity of products, the low selectivity, and the limited availability of natural sources, the site-selective reaction of multi-functional linear small molecules is still a hot topic in the field of catalysis. A suitable catalyst is required to adjust the reaction trajectories of a multi-functional linear molecule for enhancing the selectivity; it should possess both a designed active site in the channel and a uniform confined channel to restrict the molecular rotation. In recent years, nanoparticles (NPs) have been incorporated in metal-organic frameworks (MOFs) characterized with ordered nanochannel and tailorable porosity, making NPs/MOFs the outstanding candidates as the catalytic nanoreactor for heterogeneous catalysis. Herein, we developed NPs/MOFs catalysts with site-selectivity for the oxidation of diols through limiting the random rotation of the molecule within the confined space of the MOF channel. Hence, by steric hindrance, the middle -OH group was protected and only terminal -OH group was transferred to aldehydes group (in fact, the middle -OH group is more unstable than the terminal one). The above-mentioned strategy is general, which can also be extended to the site-selective reaction of other similar multi-functional linear molecules, for instance, the reduction of unsaturated aldehydes and alkadienes.

Site-selective reaction of multi-functional linear small molecules is crucial to the development of chemical synthesis¹. However, differentiating those similar functional groups with comparable activity in one molecule to achieve site selectivity remains a challenge, which usually gives rise to complex products as well as low selectivity². The low selectivity is due in part to the random rotation of the molecule in an open reaction space which offers functional groups equal opportunity to contact the catalyst³. If we apply a narrow chemical channel environment to a

linear molecule, the molecule will lose the capability of free rotation. Then, this strategy gives its end functional group a chance to contact catalytic center in the end of the channel but not the middle functional group. In Venice, there is a unique attraction called “Gondola”. The “Gondola” can change directions randomly while sailing through wide canals. When entering into the narrow “Venetian Canal”, however, the “Gondola” cannot choose but must move straight ahead due to the limited space available. Inspired by this phenomenon, we supposed that if the “Gondola” corresponding to the multi-functional linear molecule enters the narrow “Venetian Canal” corresponding to a catalyst channel, then the rotation and diffusion of molecule will be controlled in the limited space and not all functional groups can contact the active sites due to steric hindrance. Hence, a suitable catalyst featuring both a uniform channel to limit molecular rotation and the encapsulated active site to supply high reactivity would be a powerful tool for realizing site-selective reaction of multi-functional linear small molecules.

Metal-organic frameworks (MOFs)⁴⁻⁶, a new type of porous crystalline materials, have attracted research attention due to their unique porous structures and diverse compositions, and the applications of MOFs have been explored in a wide range of fields, such as gas storage⁷, gas separation⁸, chemical sensing^{9,10}, drug delivery¹¹, energy storage¹², and in particular, catalysis¹³⁻¹⁵. Indeed, using MOFs as catalysts is one of their earliest proposed¹⁶ as well as demonstrated applications¹⁷. MOFs not only share some of the relevant features of traditional zeolites catalysts¹⁸ in terms of uniform pore size and large surface area, but also offer more opportunities in terms of novel catalyst design. For example, because of the inorganic-organic bi-compositional nature of MOFs, their diverse synthetic strategies and gentle synthetic conditions, the physical, chemical and biological environments of the cages or channels within MOFs can be flexibly engineered either by the introduction of organic ligands with specific functional

groups/unsaturated metal sites during MOF growth^{19, 20} or by post-modification methods^{21, 22}. Such engineering cannot be easily realized by zeolites due to their pure inorganic nature and harsh synthetic conditions. In addition to providing an abundant pore environment, MOFs can also serve as unique hosts for the incorporation of functional species (e.g. metal nanoparticles, NP) to structure heterogeneous catalysts. Different from zeolites, MOFs can not only serve as substrates for the dispersion of NPs²³, but also perfectly encapsulate NPs within their matrices²⁴⁻²⁶. The encapsulation enables abundant possibilities for the further application of MOFs in catalysis, especially in selective catalysis, by combining the molecular sieve properties of MOFs and the catalytically active sites of NPs. Thus, MOFs will exhibit unique advantages as catalysts in fine chemistry and chemical synthesis. However, most studies of NPs/MOFs hybrid catalysts have focused on the size- or shape-selectivity of the reactants and products, while the development of site-selectivity in multifunctional linear small molecule catalytic reactions still remains in its infancy, despite the significance of site-selectivity in catalytic functionalization of molecules with multi-functional groups.

Pharmaceutical, chemical and biological molecules usually contain several similar functional groups with comparable activity²⁷, such as, hydroxy or C=C bonds, which poses a significant synthetic challenge because a highly site-selective catalyst is required to differentiate the functional groups. Enzymes^{28, 29} are the specific and effective catalysts that orient and activate substrates via specific non-covalent or steric interactions between functional groups on the catalyst and reactant to dramatically increase the selectivity of organic transformations. However, enzymes do not provide a general solution to the problem due to their demanding living environment. Consequently, the study of synthetic organic molecules for site-selective catalysis is increasingly important. Some researchers have employed directing groups or reagents to

demonstrate selective functionalization of molecules with several similar functional groups, such as, site- and enantioselective epoxidation of certain positions of polyene and the site-selective oxidation of diols^{2, 30-35}. However, both of these tools, enzymes or modified organic molecules, are often applicable to only one type of reaction. By contrast, some heterogeneous catalysts either modified with capping ligands³⁶ or encapsulated active sites^{37, 38} permit universal selective oxidation or hydrogenation by employing steric hindrance. Nevertheless, the capping ligands are restricted to thiol, oleic acid and oleylamine molecules with long chains or special metal-sulfur interaction. In addition, the encapsulation of the active within the existing catalytic carriers (zeolites, carbon and silica) is hindered by the harsh synthesis conditions³⁹. Hence, it's necessary to search for the universal catalysts that can achieve site-selective catalysis with broad reaction scopes in multi-functional linear molecules.

Herein, we report the application of a NP/MOF hybrid catalyst that can react selectively with one functional group among several similar groups in a linear small molecule by combining the pore confinement effect of MOFs and the catalytic activity of NPs. NPs encapsulated in MOFs matrixes may be referred to as "host-guest" complexes^{40, 41}. Generally, the molecule must diffuse along the MOF channel to contact the catalytic center and to activate the functional group. However, in contrast to open space, the regular and confined MOFs channel space limits the molecular movement, arrangement and rotation. Consequently, not all the functional groups can contact the catalytic sites, and site-selectivity can be achieved. In this contribution, we utilize the concept to design the pore size of NP/MOF catalysts and to demonstrate site-selective oxidation of diols and site-selective hydrogenation of alkadiene. First, in contrast to literature methods, the NP/MOF catalyst is not constrained to only one type of reaction but is also applicable to a wide range of reactions, such as oxidation reaction, hydrogenation reaction, etc. Second, in contrast to

enzymes and synthetic organic catalysts, the preparation and design of catalysts do not require a complex chemical synthesis procedure but can be achieved simply by adjusting the species of NPs and the constructed units of MOFs. To obtain a fundamental understanding of the different molecular movements in limited and open space, molecular dynamic simulation was further employed to study the penetration of diols and alkadienes across the frameworks of MOFs. The simulation results were consistent with the experimental data, further demonstrating that the site-selective reaction of multi-functional molecules can be achieved by precisely engineering the channel of NPs/MOFs.

Results

The design and structure characterization of NPs/MOFs. To realize our concept, the NP/MOF catalyst was rationally designed and synthesized. Of the three dimensional Zn- or Zr-containing MOFs known to be stable under all types of conditions, ZIF-8^{42, 43} (**Fig. 2a**) and UiO-66^{25, 44, 45} (**Fig. 2d**) were taken as examples to study site-selective catalysis. Platinum (Pt) NPs served as catalysts due to their outstanding catalytic activity⁴⁶ and Pt NPs was kept same in all catalysts (Pt/MOFs, Pt-CNT) in order to avoid effects of the Pt NPs in the catalytic reaction. In a typical synthesis, methanolic or dimethylformamide (DMF) solutions of metal salt, organic ligands and 2.9 nm Pt NPs modified with polyvinyl pyrrolidone (PVP) were briefly mixed and then kept at certain temperature for 24 h without stirring. The products, referred to as Pt/MOFs (in this case, the products are Pt/ZIF-8 and Pt/UiO-66), were collected by centrifugation and then washed with methanol or DMF. **Fig. 2b** and **Fig. 2e** present transmission electron microscopy (TEM) images of the obtained Pt/ZIF-8 and Pt/UiO-66 composites respectively, which exhibited intact crystal morphology. Notably, no aggregation of Pt NPs was observed inside the MOFs matrixes and no Pt NPs were observed on the MOFs surface. In addition, as observed in the N₂ adsorption-

desorption analysis, the steep increase in N₂ uptake at low relative pressure indicated the microporous structure of the ZIF-8 and UiO-66 crystals (**Fig. 2c, 2f**). Interestingly, the incorporation of Pt NPs did not alter the pore size distribution of the MOF matrix, therefore, Pt/ZIF-8 and Pt/UiO-66 exhibited uniform aperture sizes (ZIF-8 3.4 Å^{42, 43, 47}, UiO-66 6 Å^{44, 45}). These results indicate that, instead of occupying the MOF cavities, the introduced NPs are gradually surrounded by the growing MOFs. Based on the unique structure of NPs/MOFs, site-selective catalysis may be achieved by confining the NPs at the center of the MOFs as well as by using the limited channel of the MOFs to block reactant trajectories that lead to undesired products. Hence, oxidation of diols and hydrogenation of alkadiene were chosen as example reactions to confirm that the site-selectivity can indeed be achieved by our NP/MOF hybrid catalyst.

Site-selective oxidation of diols by using the NPs/MOFs. Site-selective oxidation is important in the synthesis of fine chemical and pharmaceutical intermediates, and in particular, the oxidation of diols to aldehydes is a fundamentally important laboratory and commercial procedure. The site-selective catalysis of diol by homogeneous catalysts^{33, 35} such as enzymes, protein and synthetic organic molecules has been studied, but the selective manipulation of several very similar reactive hydroxy groups within a molecule remains a significant challenge in the development of heterogeneous catalysis. In this case, hexan-1,5-diol, which contains one primary hydroxy group and one secondary hydroxy group, was used as an example to study selective oxidation. Each experiment was conducted over a period of up to 12 h at 393 K. For the common mechanism of alcohol oxidation on a metal surface, the hydroxy group must first adsorb on the metal surface, resulting in the formation of metal alkoxide and metal hydride; next, a hydrogen atom is removed by a surface metal atom via a *b*-hydride elimination process; finally,

the metal active site is regenerated via the oxidation of adsorbed hydrogen by molecular oxygen⁴⁸⁻⁵⁰. For the oxidation reaction of hexan-1,5-diol (**Tab. 1**), Pt NPs deposited on carbon nanotube (Pt-CNT) as a common catalyst simultaneously catalyzed the oxidation of two hydroxy groups, the primary hydroxyl to aldehyde and the secondary hydroxyl to ketone, without selectivity. These results can be attributed to the open reaction space around the Pt-CNT catalyst, which permits random molecular rotation and contact of the Pt surface by both the primary and the second hydroxy group. Encapsulation of the Pt NPs in UiO-66 with a large aperture size (6 Å) gradually increased the selectivity for primary hydroxy groups to 72.9%, much higher than that of Pt-CNT (45.1%), even though both of the hydroxy groups can still be oxidized owing to the large pore size, which is sufficiently large to permit molecular rotation. Interestingly, Pt NPs encapsulated in ZIF-8 as catalysts achieved partial oxidation of hexan-1,5-diol with 100% selectivity, i.e., only the primary hydroxyl was oxidized but not the secondary one (**Supplementary Fig. 1**). The selectivity may be attributable to small aperture size (3.4 Å) of ZIF-8 crystal, which only allowed the primary hydroxy group to touch the Pt NP surface but restrained the secondary hydroxy group from touching the Pt NPs surface. The crystal structure of the catalysts was preserved after the catalytic reactions and no degradation was detected by TEM, XRD and BET (**Supplementary Fig. 2-4**). To further confirm the concept, the oxidation reactivity of Pt/ZIF-8 toward hexan-1-ol, hexan-2-ol, and hexan-3-ol was compared (**Tab. 1**). As expected, Pt/ZIF-8 oxidized hexan-1-ol but exhibited no oxidative activity towards hexan-2-ol and hexan-3-ol, whereas Pt/UiO-66 and Pt-CNT indiscriminately oxidized all three alcohols.

Based on the above results, there may be two major reasons for the selective oxidation of diols using Pt/ZIF-8 as a catalyst (**Fig. 3**). The first is the priority of molecule diffusion into MOFs pores. The primary hydroxy group (1.9 Å) diffuses more easily through the pore apertures of the

ZIF-8 shells (3.4 Å) than the secondary hydroxy group (2.5 Å), in agreement with the results of molecular dynamic simulation (**Tab. 2**). Hence, the primary hydroxyl has priority to enter the pore apertures of ZIF-8 and touch the surface of Pt NPs. Conversely, the secondary hydroxy has low probability to enter the ZIF-8 channel because of steric effect. The second reason is the molecule arrangement in the MOF channel. The ZIF-8 pore aperture supplies sufficient space for the primary hydroxy group to diffuse and touch the Pt surface, whereas for the secondary hydroxy group, the -CH₃ may touch the Pt surface first. In the latter situation, oxidation of the secondary hydroxy group can occur only by rotation of the secondary hydroxy group and -CH₃, which is not permitted by the pore size of ZIF-8. Hence, even though the secondary hydroxy group enters the ZIF-8 pore apertures, the oxidation reaction can rarely occur because of the lack of space for secondary hydroxy rotation. By contrast, the UiO-66 shell has a larger pore size (6 Å), which provides the space required for the rotation of the secondary hydroxy group and -CH₃ without serious hindrance. Thus, Pt/UiO-66 exhibits catalytic activity for the oxidation of both primary and secondary hydroxy groups.

To confirm the above hypothesis, a molecular dynamic simulation was employed to study the penetration of the hexan-1,5-diol molecule across the frameworks of ZIF-8 and UiO-66, and to obtain a fundamental understanding of the molecular movement in limited space and open space. Detailed information on the crystal data of the MOFs, structural information for the organic molecule, and the simulation conditions are described in the supporting information (**Supplementary Tabs. 8-9**). The crystal structures of ZIF-8 and UiO-66 were determined using a computationally assisted procedure with a unit cell of 8×8×8 for ZIF-8 and 2×2×2 for UiO-66. First, 200 molecules of hexan-1,5-diol were taken as an example to study the priority of molecule diffusion into ZIF-8. As shown in **Tab. 2**, the primary hydroxy group (A-OH) has a

much higher tendency (88.8%) to diffuse into the ZIF-8 framework than the secondary hydroxy group (B-OH, 11.2%), corroborating our assumption that A-OH, with smaller steric hindrance than B-OH, can more easily enter the ZIF-8 framework. In addition, the snapshot of the penetration of hexan-1,5-diol in ZIF-8 also demonstrated that most of the hexan-1,5-diol molecules are arranged with the A-OH end downwards and the B-OH end upwards (**Tab. 2**). This simulation result corresponds well with the hypothesized priority of molecule diffusion into MOF pores. However, among the two sides -CH₃ (B-CH₃) and B-OH, which one will diffuse into ZIF-8 first is an intriguing issue yet to be figured out. Through analysis of the sequence of B-CH₃ and B-OH, B-CH₃ has 100% priority to diffuse into the ZIF-8 frameworks compared to B-OH. These simulation results are consistent with our experimental results: the primary hydroxy group has 100% selectivity for penetration across the ZIF-8 framework. For UiO-66, 100 molecules of hexan-1,5-diol were employed to study the penetration process (**Tab. 2**), which revealed much lower selectivity (63.6%) in the priority of molecule diffusion, probably due to the larger pore size of UiO-66 (**Supplementary Fig. 5**). Furthermore, analysis of the 36.4% molecules in which the secondary hydroxy group diffused first revealed that only the 12.4% of B-OH diffuse out of UiO-66 frameworks prior to B-CH₃. Although the simulation result (12.4%) is lower than the experiment result (27%) in the selectivity of the secondary hydroxy group, it still serves as a strong evidence that the large pore size permits random rotation of molecules and leads to the poor selectivity between the primary and secondary hydroxy group in hexan-1,5-diol molecules. Hence, the designable and tunable pore size of MOFs is essential for site-selective oxidation of diol. In addition to the preparation of various MOFs with different pores, the pore size and pore environment of as-prepared MOFs can be designed and adjusted by using a post-

modification method, indicating that the versatility of NPs/MOFs can be utilized for a broad range of applications in the field of site-selective catalysis.

Site-selective hydrogenation of alkadiene by using the NPs/MOFs. In addition to selective oxidation, selective hydrogenation of one part of bifunctional linear small molecules is also a fundamental challenge in heterogeneous catalysis. Thereofre, achievement of site-selective hydrogenation reaction via the simple physical limitation of the pore size of Pt/ZIF-8 would have a huge impact. A model diene reactant, (*E*)-hex-1,4-diene, was employed as an example in selective hydrogenation reaction. In the absence of the ZIF-8 shell, Pt NPs simultaneously catalyzed the hydrogenation of two C=C double bonds to produce hexane at 35 °C for 24 h under static conditions. Once encapsulated, Pt/ZIF-8 as catalyst partially hydrogenated (*E*)-hex-1,4-diene to (*E*)-hex-2-ene and exhibited no activity on secondary C=C double bonds (**Tab. 3**). The results are similar to the oxidation of diol: the small aperture size of ZIF-8 does not allow random rotation of the molecules. As a result, only the terminal C=C group can be transformed into the C-C group, and the middle C=C functional group is protected by the simple physical limitation of MOF's pore apertures. In addition, Pt/ZIF-8 composites were evaluated for the comparative hydrogenation reactions of pent-1-ene, (*E*)-pent-2-ene, and (*E*)-hex-3-ene (**Tab. 3**). The results were consistent with those of the above described experiment. In additon, Pt/ZIF-8 exhibited activity for pent-1-ene but no activity for the hydrogenation of the C=C double bond at the second or third carbon in the olefins. The higher conversion of hydrogenation of pent-1-ene than that of hex-1-ene¹⁶ was probably due to the smaller size of pent-1-ene and, consequently, its faster diffusion rate. Both Pt/Uio-66 and Pt-CNT indiscriminately catalyzed the hydrogenation of all olefins because of their large pore sizes and low steric hindrance (**Supplementary Fig. 5**).

The crystal structure and microporous nature of the catalysts were preserved after reaction, with no degradation detected by TEM, XRD and BET (**Supplementary Fig. 8-10**).

Compared with hexan-1,5-diol (88.8%), the side C=C group of the (*E*)-hex-1,4-diene molecules have lower priority (70.8%) to enter the ZIF-8 pore aperture, probably due to the similar steric hindrance of terminal-CH₃ (B-CH₃) and terminal -CH₂ (A-CH₂) (**Supplementary Tab. 3**). The results can also be demonstrated by the snapshot of the penetration of (*E*)-hex-1,4-diene in ZIF-8 and UiO-66 (**Supplementary Fig. 10-11**). The difference between the terminal C=C and the secondary C=C is the molecular arrangement in the limited space (**Supplementary Fig. 7**). The terminal C=C can diffuse through the pore apertures of ZIF-8 and directly contact the Pt surface, resulting in reaction. If the secondary C=C enters the ZIF-8 pore aperture, then the -CH₃ touches the Pt surface first, as confirmed by the simulation results which indicate that 100% of -CH₃ diffuse out of the ZIF-8 framework prior to the secondary C=C group. In this situation, hydrogenation of secondary C=C can occur only by rotation of the (*E*)-hex-1,4-diene molecules and adsorption of the secondary C=C bond. However, the ZIF-8 pore size is not sufficiently large for rotation of the molecule. Hence, even if the secondary C=C end enters the ZIF-8 pore apertures, the hydrogenation reaction cannot occur. The selective hydrogenation reaction can also be achieved by incorporation of the NPs in a MOF matrix with tunable pore sizes.

Site-selective hydrogenation of unsaturated aldehydes by using the NPs/MOFs. This concept of site-selectivity can also be verified by the selective hydrogenation of unsaturated aldehydes. The molecule (*Z*)-hept-4-enal, which has C=O and C=C bifunctional groups, was also taken as an example to study the site-selective catalysis. Pt/ZIF-8 as the catalyst partially hydrogenated (*Z*)-hept-4-enal to (*Z*)-hept-4-en-1-ol and showed no activity on the third C=C double bond

(Supplementary Tab. 5). These results are in agreement with the selective oxidation of diols and the selective hydrogenation of alkadiene. Therefore, in addition to the selective oxidation reaction of diols, the selective hydrogenation reaction of alkadienes and unsaturated aldehydes can be achieved by engineering the MOF channels to sterically hinder the middle functional group, indicating the wide possible reaction scopes of our proposed NPs/MOFs hybrid catalysts.

Discussion

In summary, we have demonstrated the concept that a simple heterogeneous catalyst, NPs/MOFs, can perform site-selective catalysis for the formation of a single product from bifunctional linear small molecules by suitably engineering the pore size and pore environment of the MOFs. Pt/ZIF-8, as a heterogeneous catalyst, provides site-selectivity for oxidation of diols and hydrogenation of alkadienes and unsaturated aldehydes based on protection of the secondary functional group by the simple physical space limitation of the MOF pores. Moreover, the penetration of diol and alkadiene molecules in the MOF channels was analyzed by molecular dynamic simulation, which confirmed the experimental results and the proposed concepts. Developing NPs/MOFs as a catalyst for site-selective catalysis to obtain a single product by using microporous MOFs to block reactant trajectories that lead to undesired products is a state-of-the-art development for heterogeneous catalysis. Furthermore, the concept described herein is not only suitable to the field of catalysis, but also offers a new perspective to overcome an acknowledged difficulty (selective activity of C-H bond) in organic synthesis and pharmaceutical preparation.

References

- 296 1. Beauchemin, A.M. Site-selective reactions: exploiting intramolecularity. *Nat. Chem.* **5**,
297 731-732 (2013).
- 298 2. Lichtor, P.A. & Miller, S.J. Combinatorial evolution of site- and enantioselective catalysts
299 for polyene epoxidation. *Nat. Chem.* **4**, 990-995 (2012).
- 300 3. Li M.Y., Gonzalez-Esguevillas M., Berritt S., Yang X.D., Bellomo A., Walsh P.J.
301 Palladium-Catalyzed C-H Arylation of alpha,beta-Unsaturated Imines: Catalyst-
302 Controlled Synthesis of Enamine and Allylic Amine Derivatives. *Angew. Chem. Int. Edit.*
303 **8**, 2825-2829 (2016).
- 304 4. Horike, S., Shimomura, S. & Kitagawa, S. Soft porous crystals. *Nat. Chem.* **1**, 695-704
305 (2009).
- 306 5. Ferey, G. Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* **37**, 191-214
307 (2008).
- 308 6. Furukawa, H. et al. Ultrahigh porosity in metal-organic frameworks. *Science* **329**, 424-
309 428 (2010).
- 310 7. Rosi, N.L. et al. Hydrogen storage in microporous metal-organic frameworks. *Science*
311 **300**, 1127-1129 (2003).
- 312 8. Li, J.R., Kuppler, R.J. & Zhou, H.C. Selective gas adsorption and separation in metal-
313 organic frameworks. *Chem. Soc. Rev.* **38**, 1477-1504 (2009).
- 314 9. Kreno, L.E. et al. Metal-organic framework materials as chemical sensors. *Chem. Rev.*
315 **112**, 1105-1125 (2011).
- 316 10. He, L. et al. Core-shell noble-metal@metal-organic-framework nanoparticles with highly
317 selective sensing property. *Angew. Chem. Int. Edit.* **52**, 3741-3745 (2013).

- 318 11. Horcajada, P. et al. Porous metal-organic-framework nanoscale carriers as a potential
319 platform for drug delivery and imaging. *Nat. Mater.* **9**, 172-178 (2010).
- 320 12. Wu, H.B., Xia, B.Y., Yu, L., Yu, X.-Y. & Lou, X.W. Porous molybdenum carbide nano-
321 octahedrons synthesized via confined carburization in metal-organic frameworks for
322 efficient hydrogen production. *Nat. Commun.* **6**, 6512 (2015).
- 323 13. Lee, J. et al. Metal-organic framework materials as catalysts. *Chem. Soc. Rev.* **38**, 1450-
324 1459 (2009).
- 325 14. Jiang, H.-L., Akita, T., Ishida, T., Haruta, M. & Xu, Q. Synergistic catalysis of Au@Ag
326 core-shell nanoparticles stabilized on metal-organic framework. *J. Am. Chem. Soc.* **133**,
327 1304-1306 (2011).
- 328 15. Zhao, M. et al. Metal-organic frameworks as selectivity regulators for hydrogenation
329 reactions *Nature* **539**, 76-80 (2016).
- 330 16. Hoskins, B.F. & Robson, R. Design and construction of a new class of scaffolding-like
331 materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A
332 reappraisal of the zinc cyanide and cadmium cyanide structures and the synthesis and
333 structure of the diamond-related frameworks $[N(CH_3)_4][Cu(I)Zn(II)(CN)_4]$ and
334 $CuI[4,4',4'',4''']$ -tetracyanotetraphenylmethane]BF₄.x C₆H₅NO₂. *J. Am. Chem. Soc.* **112**,
335 1546-1554 (1990).
- 336 17. Fujita, M., Kwon, Y.J., Washizu, S. & Ogura, K. Preparation, Clathration Ability, and
337 Catalysis of a Two-Dimensional Square Network Material Composed of Cadmium(II)
338 and 4,4'-Bipyridine. *J. Am. Chem. Soc.* **116**, 1151-1152 (1994).
- 339 18. Tao, Y.S., Kanoh, H., Abrams, L. & Kaneko, K. Mesopore-modified zeolites: Preparation,
340 characterization, and applications. *Chem. Rev.* **106**, 896-910 (2006).

19. Deng, H.X. et al. Large-pore apertures in a series of metal-organic frameworks. *Science* **336**, 1018-1023 (2012).
20. Vermoortele, F. et al. Synthesis modulation as a tool to increase the catalytic activity of metal-organic frameworks: the unique case of UiO-66(Zr). *J. Am. Chem. Soc.* **135**, 11465-11468 (2013).
21. Cohen, S.M. Postsynthetic methods for the functionalization of metal-organic frameworks. *Chem. Rev.* **112**, 970-1000 (2011).
22. Zhang, W. et al. Mesoporous metal-organic frameworks with size-, shape-, and space-distribution-controlled pore structure. *Adv. Mater.* **27**, 2923-2929 (2015).
23. Yang, Q., Chen, Y.Z., Wang, Z.U., Xu, Q. & Jiang, H.L. One-pot tandem catalysis over Pd@MIL-101: boosting the efficiency of nitro compound hydrogenation by coupling with ammonia borane dehydrogenation. *Chem. Commun.* **51**, 10419-10422 (2015).
24. Lu, G. et al. Imparting functionality to a metal-organic framework material by controlled nanoparticle encapsulation. *Nat. Chem.* **4**, 310-316 (2012).
25. Zhang, W. et al. A Family of Metal-organic frameworks exhibiting size-selective catalysis with encapsulated noble-metal nanoparticles. *Adv. Mater.* **26**, 4056-4060 (2014).
26. Kuo, C.H. et al. Yolk-shell nanocrystal@ZIF-8 nanostructures for gas-phase heterogeneous catalysis with selectivity control. *J. Am. Chem. Soc.* **134**, 14345-14348 (2012).
27. Mahatthananchai, J., Dumas, A.M. & Bode, J.W. Catalytic selective synthesis. *Angew. Chem. Int. Edit.* **51**, 10954-10990 (2012).

- 362 28. Therisod, M. & Klibanov, A.M. Regioselective acylation of secondary hydroxyl groups in
363 sugars catalyzed by lipases in organic solvents. *J. Am. Chem. Soc.* **109**, 3977-3981
364 (1987).
- 365 29. Ringe, D. & Petsko, G.A. How enzymes work. *Science* **320**, 1428-1429 (2008).
- 366 30. Breslow, R. et al. Remote oxidation of steroids by photolysis of attached benzophenone
367 groups. *J. Am. Chem. Soc.* **95**, 3251-3262 (1973).
- 368 31. Breslow, R. & Heyer, D. Catalytic multiple template-directed steroid chlorinations. *J. Am.*
369 *Chem. Soc.* **104**, 2045-2046 (1982).
- 370 32. Tan, K.L. Induced intramolecularity: an effective strategy in catalysis. *ACS Catal.* **1**, 877-
371 886 (2011).
- 372 33. Sun, X.X., Lee, H., Lee, S. & Tan, K.L. Catalyst recognition of cis-1,2-diols enables site-
373 selective functionalization of complex molecules. *Nat. Chem.* **5**, 790-795 (2013).
- 374 34. Tanabe K.K., Ferrandon M.S., Siladke N.A., Kraft S.J., Zhang G.H., Niklas J., et al.
375 Discovery of Highly Selective Alkyne Semihydrogenation Catalysts Based on First-Row
376 Transition-Metallated Porous Organic Polymers. *Angew. Chem. Int. Edit.* **45**, 12055-
377 12058 (2014).
- 378 35. Worthy, A.D., Sun, X. & Tan, K.L. Site-selective catalysis: toward a regiodivergent
379 resolution of 1,2-diols. *J. Am. Chem. Soc.* **134**, 7321-7324 (2012).
- 380 36. Marshall, S.T. et al. Controlled selectivity for palladium catalysts using self-assembled
381 monolayers. *Nat. Mater.* **9**, 853-858 (2010).
- 382 37. Wen Z.K., Xu Y.H., Loh T.P. Palladium(ii)-catalyzed cross-coupling of simple alkenes
383 with acrylates: a direct approach to 1,3-dienes through C-H activation. *Chem. Sci.* **12**,
384 4520-4524 (2013).

- 385 38. Robinson J.R., Carroll P.J., Walsh P.J., Schelter E.J. The impact of ligand reorganization
386 on cerium(III) oxidation chemistry. *Angew. Chem. Int. Edit.* **40**, 10159-10163 (2012).
- 387 39. Wan, Y., Yang, H.F. & Zhao, D.Y. "Host-guest" chemistry in the synthesis of ordered
388 nonsiliceous mesoporous materials. *Acc. Chem. Res.* **39**, 423-432 (2006).
- 389 40. Liu Y.L., Tang Z.Y. Multifunctional nanoparticle@MOF core-shell nanostructures. *Adv.*
390 *Mater.* **40**, 5819-5825 (2013).
- 391 41. Shieh F.K., Wang S.C., Yen C.I., Wu C.C., Dutta S., Chou L.Y., et al. Imparting
392 functionality to biocatalysts via embedding enzymes into nanoporous materials by a de
393 novo approach: size-selective sheltering of catalase in metal-organic framework
394 microcrystals. *J. Am. Chem. Soc.* **13**, 4276-4279 (2015).
- 395 42. Phan, A. et al. Synthesis, structure, and carbon dioxide capture properties of zeolitic
396 imidazolate frameworks. *Acc. Chem. Res.* **43**, 58-67 (2010).
- 397 43. Huang, X., Zhang, J. & Chen, X. [Zn(bim)₂](H₂O)_{1.67}: a metal-organic open-framework
398 with sodalite topology. *Chinese Sci. Bull.* **48**, 1531-1534 (2003).
- 399 44. Kandiah, M. et al. Synthesis and stability of tagged UiO-66 Zr-MOFs. *Chem. Mater.* **22**,
400 6632-6640 (2010).
- 401 45. Guillerm, V. et al. A series of isorecticular, highly stable, porous zirconium oxide based
402 metal-organic frameworks. *Angew. Chem. Int. Edit.* **51**, 9267-9271 (2012).
- 403 46. Chen, A. & Holt-Hindle, P. Platinum-based nanostructured materials: synthesis,
404 properties, and applications. *Chem. Rev.* **110**, 3767-3804 (2010).
- 405 47. Park, K.S. et al. Exceptional chemical and thermal stability of zeolitic imidazolate
406 frameworks. *Proc. Nati. Acad. Sci.* **103**, 10186-10191 (2006).

- 407 48. Xu, B., Liu, X., Haubrich, J. & Friend, C.M. Vapour-phase gold-surface-mediated
408 coupling of aldehydes with methanol. *Nat. Chem.* **2**, 61-65 (2010).
- 409 49. Rodriguez, P., Kwon, Y. & Koper, M.T.M. The promoting effect of adsorbed carbon
410 monoxide on the oxidation of alcohols on a gold catalyst. *Nat. Chem.* **4**, 177-182 (2012).
- 411 50. Zope, B.N., Hibbitts, D.D., Neurock, M. & Davis, R.J. Reactivity of the gold/water
412 interface during selective oxidation catalysis. *Science* **330**, 74-78 (2010).

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422 **Author Contributions**

423 W.Z. and B.Z. designed the experiments, performed&analyzed the results, and drafted the
424 manuscript. W.S. and S.L. was responsible for the molecular dynamic simulation. Z.X. was
425 responsible for the nanoparticles synthesis. X.C. was responsible for the TEM characterization.
426 Y.C. performed the NMR analysis. Y.Y. supplied the facilities for the catalysis experiments.
427 W.H. J.L. and F.H. supervised the project, helped design the experiments, and revised the
428 manuscript. All authors contributed to the analysis of the manuscript.

429 **Author Information**

430 Supplementary information is available in the online version of the paper. Reprints and
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433 **Competing financial interests**

434 The authors declare no competing financial interest

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Figure legends

Figure 1 | Schematic representation of the site-selective catalysis of multi-functional linear molecule. The multi-functional linear molecule corresponds to the “Gondola” and the each channel of the MOF corresponds to a narrow “Venetian Canal”. When the “Gondola” sails into a narrow “Venetian Canal”, it can only proceed directly ahead because the narrow canal does not supply sufficient space for rotation of the “Gondola”. Hence, even though the side of the middle group enters the MOF pore apertures, reaction rarely occurs because of the lack of space for the middle group rotation.

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460

461 **Figure 2 | The structure of Pt/ZIF-8 and Pt UiO-66. a and d** the crystal structure of ZIF-8 and
 462 UiO-66, respectively. **b and e** the TEM images of Pt/ZIF-8 and Pt UiO-66, respectively. **c and f**
 463 N₂-adsorption-desorption isotherms of Pt/ZIF-8 and Pt UiO-66, respectively, at 77 K.

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471 **Table 1** | Comparison of the selectivity of the Pt/ZIF-8, Pt/UiO-66, and Pt-CNT as catalysts for
 472 hexan-1,5-diol oxidation of the corresponding aldehydes.

473

Reactant	Catalyst	Product	Conversion (%)	Selectivity(%)	
				1	2
Hexan-1,5-diol	Pt/ZIF-8		29 ± 0.1	100	0
	Pt/UiO-66		29 ± 0.2	73 ± 0.1	27 ± 0.1
	Pt-CNT		24 ± 0.3	45 ± 0.1	55 ± 0.1
Hexan-1-ol	Pt/ZIF-8	Hexanal	13 ± 0.1		
	Pt/UiO-66		21 ± 0.3		
	Pt-CNT		37
Hexan-2-ol	Pt/ZIF-8	Hexan-2-one	0		
	Pt/UiO-66		11 ± 0.2		
	Pt-CNT		22 ± 0.3
Hexan-3-ol	Pt/ZIF-8	Hexan-3-one	0		
	Pt/UiO-66		10 ± 0.2		
	Pt-CNT		21 ± 0.5		

474 Reaction condition: reactants 50 uL, Toluene 15 uL and oxygen 15 bar. Reactions were
 475 performed in toluene at 120 °C for 12 h. Detailed reaction conditions are given in the
 476 supplementary information.

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478

479 **Figure 3 | Schematic illustration of the selective oxidation of hexan-1,5-diol.** The ZIF-8 and
 480 UiO-66 pore apertures all allow the primary -OH group to enter and touch the surface of Pt NPs.
 481 However, when the secondary -OH group of the hexan-1,5-diol diffuses into the MOF pore
 482 apertures, the UiO-66 pore aperture is sufficiently large to permit the rotation, thereby allowing
 483 the secondary -OH group to touch the surface of Pt NPs. Conversely, the ZIF-8 pore apertures
 484 do not provide sufficient space for rotation of the secondary -OH group, thereby protecting the
 485 secondary -OH group.

486

Table 2 | Experimental and simulation data of the penetration ratio for hexan-1,5-diol in ZIF-8 and UiO-66, and a snapshot of the penetration of hexan-1, 5-diol (200 molecules) in ZIF-8.

Diols	MOFs	Experimental		Simulation		
		A-OH	B-OH	A-OH	B-CH ₃	B-OH
<p>Hexan-1,5-diol</p>	ZIF-8 (3.4 Å)	100%	0	88.8%	11.2%	0
	UiO-66 (6 Å)	73%	27%	66%	21.6%	12.4%

Table 3 | Comparison of the selectivity of the Pt/ZIF-8, Pt UiO-66, and Pt-CNT as catalysts for (E)-hex-1,4-diene hydrogenation to the corresponding alkanes.

Reactants	Catalysts	Products	Conversion (%)	Selectivity (%)			
				1	2	3	4
 (E)-hex-1,4-diene	Pt/ZIF-8	 (E)-hex-2-ene	27 ± 0.3	100	0	0	0
	Pt/UiO-66		100	38 ± 0.3	60 ± 0.5	0	2 ± 0.5
	Pt-CNT		100	20 ± 0.5	75 ± 0.2	5 ± 0.3	0
 Pent-1-ene	Pt/ZIF-8	 Pentane	33 ± 0.1				
	Pt/UiO-66		100				
	Pt-CNT		100				
 (E)-pent-2-ene	Pt/ZIF-8	 Pentane	0				
	Pt/UiO-66		100				
	Pt-CNT		100				
 (E)-hex-3-ene	Pt/ZIF-8	 Hexane	0				
	Pt/UiO-66		100				
	Pt-CNT		100				

Reaction Condition: Reactants 100 uL, Ethyl acetate 3 mL, and Hydrogen 1atm. Reaction were performed in ethyl acetate at 35 °C for 24 h. Detailed reaction conditions are given in the supplementary information.