

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

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The site-selective reaction of a multifunctional linear molecule requires a suitable catalyst possessing both uniform narrow channel to limit the molecule rotation and a designed active site in the channel. Recently, nanoparticles (NPs) were incorporated in metal–organic frameworks (MOFs) with the tailorable porosity and ordered nanochannel, which makes these materials (NPs/MOFs) highly promising candidates as catalytic nanoreactors in the field of heterogeneous catalysis. Inspired by a “Gondola” sailing in narrow “Venetian Canal” without sufficient space for a U-turn, a simple heterogeneous catalyst based on NPs/MOFs is developed that exhibits site-selectivity for the oxidation of diols by restricting the random rotation of the molecule (the “Gondola”) in the limited space of the MOF channel (the narrow “Venetian Canal”), thereby protecting the middle functional group via steric hindrance. This strategy is not limited to the oxidation of diols, but can be extended to the site-selective reaction of many similar multifunctional linear molecules, such as the reduction of alkadienes.

Site-selective reaction of multifunctional linear small molecules is crucial to the development of chemical synthesis.^[1–4] 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 selectivity.^[5–7] 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 catalyst.^[8–10] 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. Hence, a suitable catalyst featuring both 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 multifunctional linear small molecules.

Metal–organic frameworks (MOFs),^[11–13] 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 storage,^[14] gas separation,^[15,16] chemical sensing,^[17,18] drug delivery,^[19] energy storage,^[20] and in particular, catalysis.^[21–24] Indeed, using MOFs as catalysts is one of their earliest proposed^[25] as well as demonstrated applications.^[26] MOFs not only share some of the relevant features of traditional zeolites catalysts^[27] 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 bicompositional 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^[28,29] or by postmodification methods.^[30,31] 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, NPs) to structure heterogeneous catalysts. Different from zeolites, MOFs can not only serve as substrates for the dispersion of NPs^[32] but also perfectly encapsulate NPs within their matrices.^[33–35] The encapsulation enables

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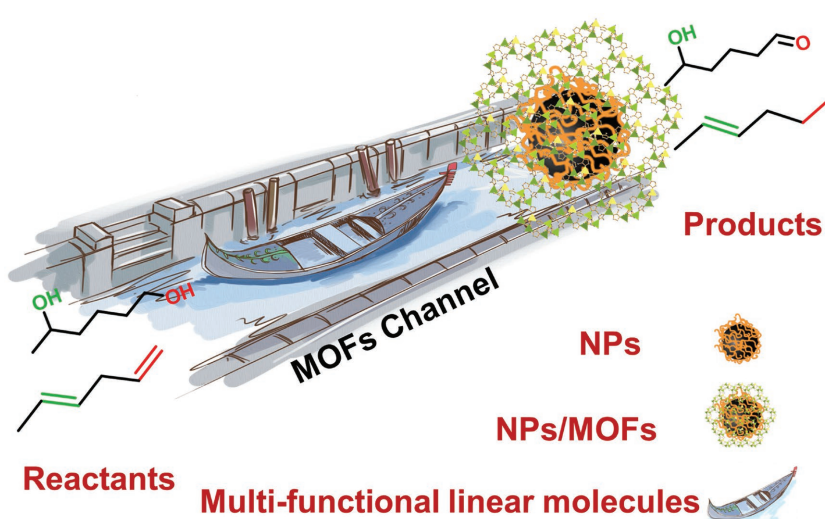
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abundant possibilities for the further application of MOFs in catalysis, especially in selective catalysis, by combining the molecular sieve properties of MOFs and the catalytically active sites of NPs. Thus, MOFs will exhibit unique advantages as 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 multifunctional groups.

Pharmaceutical, chemical, and biological molecules usually contain several similar functional groups with comparable activity,^[1,2] such as hydroxyl or C=C bonds, which poses a significant synthetic challenge because a highly site-selective catalyst is required to differentiate the functional groups. Enzymes^[36,37] are the specific and effective catalysts that orient and activate substrates via specific noncovalent 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^[9,38] 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.^[3,7,39] 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 ligands^[10] or encapsulated active sites^[40,41] 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 conditions.^[42] Hence, it is necessary to search for the universal catalysts that can achieve site-selective catalysis with broad reaction scopes in multifunctional 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.^[43,44] 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



Scheme 1. Schematic representation of the site-selective catalysis of multifunctional linear molecule. The multifunctional linear molecule corresponds to the “Gondola” and 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.

rotation. Consequently, not all the functional groups can contact the catalytic sites, and site-selectivity can be achieved. The phenomenon is similar to the “Gondola” sailing into a narrow “Venetian Canal” in which the “Gondola” cannot freely rotate to change directions. 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 (**Scheme 1**). First, in contrast to literature methods, the NP/MOF catalyst is not only constrained to one type of reaction but 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 multifunctional molecules can be achieved by precisely engineering the channel of NPs/MOFs.

To realize our concept, the NP/MOF catalyst was rationally designed and synthesized. Of the 3D Zn- or Zr-containing MOFs known to be stable under all types of conditions, ZIF-8^[45,46] (**Figure 1a**) and UiO-66^[34,47,48] (**Figure 1d**) were taken as examples to study site-selective catalysis. Platinum (Pt) NPs served as catalysts due to their outstanding catalytic activity^[49] and Pt NPs were 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

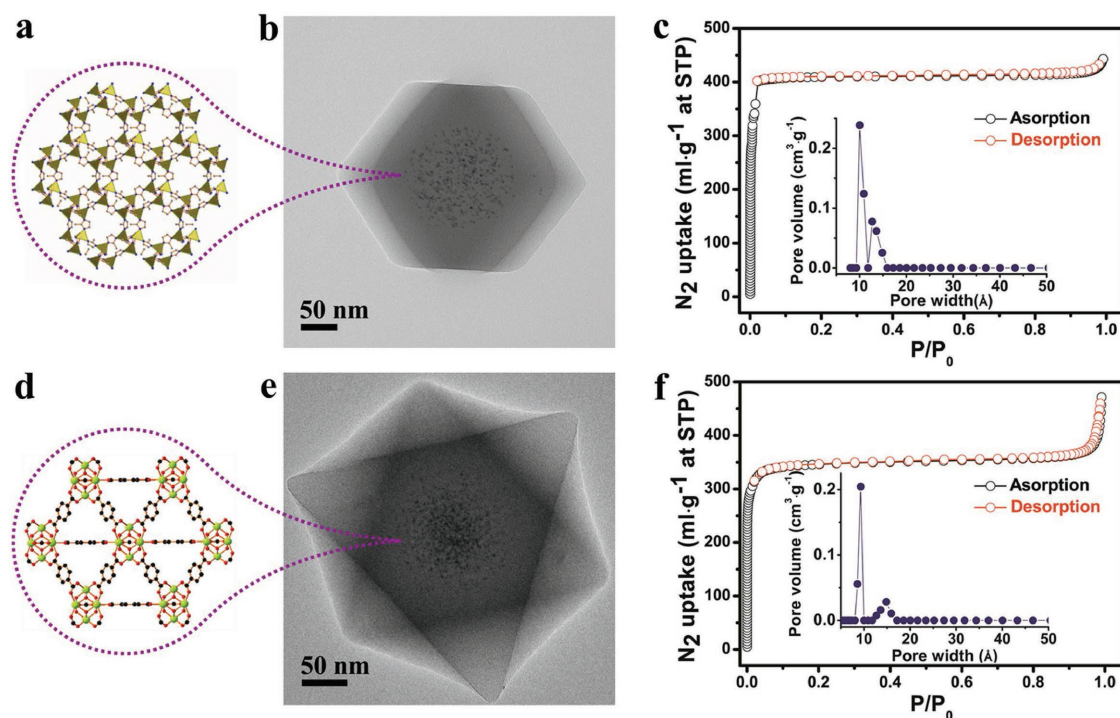


Figure 1. The structure of Pt/ZIF-8 and Pt/Uio-66. a,d) The crystal structure of ZIF-8 and Uio-66, respectively. b,e) The TEM images of Pt/ZIF-8 and Pt/Uio-66, respectively. c,f) N_2 adsorption–desorption isotherms of Pt/ZIF-8 and Pt/Uio-66, respectively, at 77 K.

modified with poly(vinylpyrrolidone) (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. Figure 1b,e presents 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 N_2 adsorption–desorption analysis, the steep increase in N_2 uptake at low relative pressure indicated the microporous structure of the ZIF-8 and Uio-66 crystals (Figure 1c,f). 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,^[45,46,50] Uio-66 6 Å^[47,48]). 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 alkadienes were chosen as example reactions to confirm that the site-selectivity can indeed be achieved by our NP/MOF hybrid catalyst.

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^[3,5] 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 β -hydride elimination process; finally, the metal active site is regenerated via the oxidation of adsorbed hydrogen by molecular oxygen.^[51–53] For the oxidation reaction of hexan-1,5-diol (Table 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, that is, only the primary hydroxyl was oxidized but not the secondary one. The selectivity may be attributable to small aperture size (3.4 Å) of ZIF-8 crystal, which only allowed

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

Reactant ^{a)}	Catalyst	Product	Conversion [%]	Selectivity [%]	
				1	2
 Hexan-1,5-diol	Pt/ZIF-8	 5-hydroxyhexanal	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		

^{a)}Reaction condition: reactants 50 μ L, toluene 15 μ L, and oxygen 15 bar. Reactions were performed in toluene at 120 $^{\circ}$ C for 12 h. Detailed reaction conditions are given in the Supporting Information.

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 Brunauer–Emmett–Teller (BET) (Figures S1–S3, Supporting Information). 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 (Table 1). As expected, Pt/ZIF-8 oxidized hexan-1-ol but exhibited no oxidative activity toward 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 (Figure 2). The first is the priority of molecule diffusion into MOFs pores. The primary hydroxy (–OH) group (1.9 Å) diffuses more easily through the pore apertures of the ZIF-8 shells (3.4 Å) than the secondary hydroxy (–OH) group (2.5 Å), in agreement with the results of molecular dynamic simulation (Table 2). Hence, the primary hydroxyl (–OH) has priority

to enter the pore apertures of ZIF-8 and touch the surface of Pt NPs. Conversely, the secondary hydroxy (–OH) 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 (–OH) group to diffuse and touch the Pt surface, whereas for the secondary hydroxy (–OH) group, the –CH₃ may touch the Pt surface first. In the latter situation, oxidation of the secondary hydroxy (–OH) group can occur only by rotation of the secondary hydroxy (–OH) group and –CH₃, which is not permitted by the pore size of ZIF-8. Hence, even though the secondary hydroxy (–OH) group enters the ZIF-8 pore apertures, the oxidation reaction can rarely occur because of the lack of space for secondary hydroxyl (–OH) 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 (–OH) group and –CH₃ without serious hindrance. Thus, Pt/UiO-66 exhibits catalytic activity for the oxidation of both primary and secondary hydroxy groups.

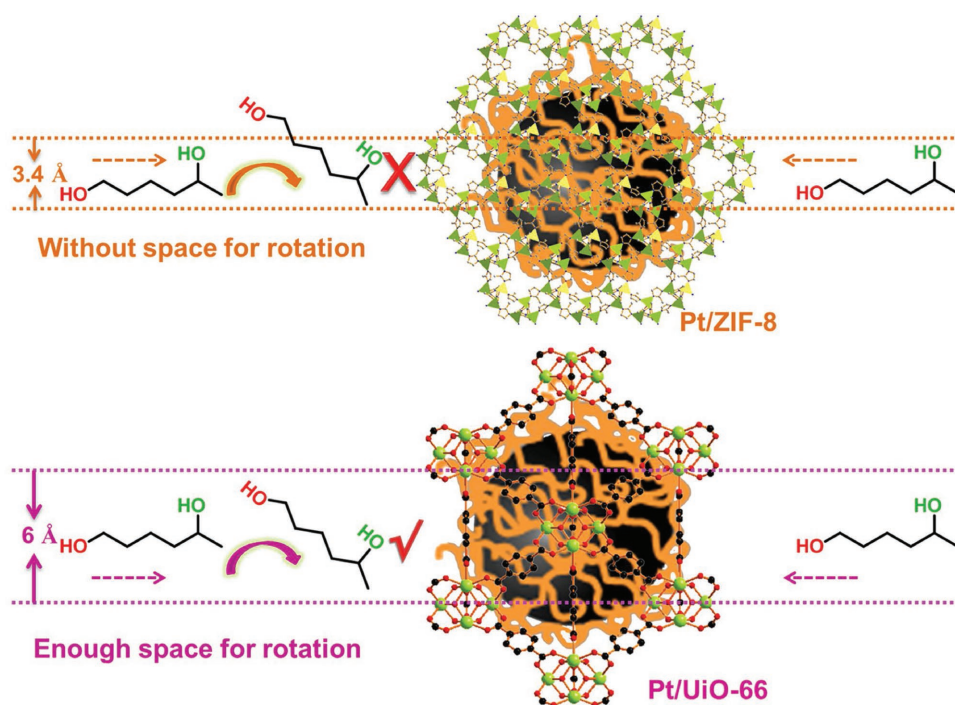


Figure 2. Schematic illustration of the selective oxidation of hexan-1,5-diol. The ZIF-8 and UiO-66 pore apertures all allow the primary --OH group to enter and touch the surface of Pt NPs. However, when the secondary --OH group of the hexan-1,5-diol diffuses into the MOF pore apertures, the UiO-66 pore aperture is sufficiently large to permit the rotation, thereby allowing the secondary --OH group to touch the surface of Pt NPs. Conversely, the ZIF-8 pore apertures do not provide sufficient space for rotation of the secondary --OH group, thereby protecting the secondary --OH group.

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 of the organic molecule, and the simulation conditions are described in Tables S4 and S6 (Supporting Information).

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.

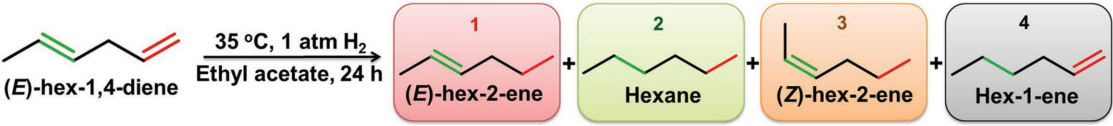
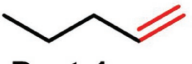
Diols	MOFs	Experimental		Simulation		
Hexan-1,5-diol	ZIF-8 (3.4 Å)	A-OH	B-OH	A-OH	B-CH ₃	B-OH
	UiO-66 (6 Å)	100%	0	88.8%	11.2%	0
		73%	27%	66%	21.6%	12.4%

The crystal structures of ZIF-8 and UiO-66 were determined using a computationally assisted procedure with a unit cell of $8 \times 8 \times 8$ for ZIF-8 and $2 \times 2 \times 2$ 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 Table 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 downward and the B–OH end upward (Table 2). This simulation result corresponds well with the hypothesized priority of molecule diffusion into MOF pores. However, among the two sides $-\text{CH}_3$ (B– CH_3) 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– CH_3 and B–OH, B– CH_3 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 (Table 2), which revealed much lower selectivity (63.6%) in the priority of molecule diffusion, probably due to the larger pore size of UiO-66

(Figure S4, Supporting Information). 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– CH_3 . 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 postmodification method, indicating that the versatility of NPs/MOFs can be utilized for a broad range of applications in the field of site-selective catalysis.

In addition to selective oxidation, selective hydrogenation of one part of bifunctional linear small molecules is also a fundamental challenge in heterogeneous catalysis. Therefore, 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.

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 ^{a)}	Catalysts	Products	Conversion	Selectivity [%]			
[%]				1	2	3	4
 (<i>E</i>)-hex-1,4-diene	Pt/ZIF-8		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				
 (<i>E</i>)-pent-2-ene	Pt/ZIF-8	 Pentane	0				
	Pt/UiO-66		100				
	Pt-CNT		100				
 (<i>E</i>)-hex-3-ene	Pt/ZIF-8	 Hexane	0				
	Pt/UiO-66		100				
	Pt-CNT		100				

^{a)} Reaction condition: reactants 100 μL, ethyl acetate 3 mL, and hydrogen 1 atm. Reactions were performed in ethyl acetate at 35 °C for 24 h. Detailed reaction conditions are given in the Supporting Information.

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 (Table 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, pent-2-ene, and hex-3-ene (Table 3). The results were consistent with those of the above described experiment. In addition, 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-ene^[25] 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 (Figure S5, Supporting Information). The crystal structure and microporous nature of the catalysts were preserved after reaction, with no degradation detected by TEM, XRD, and BET (Figures S6–S8, Supporting Information).

Compared with hexan-1,5-diol (88.8%), the side C=C group of the (*E*)-hex-1,4-diene molecules has 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) (Table S3, Supporting Information). The results can also be demonstrated by the snapshot of the penetration of (*E*)-hex-1,4-diene in ZIF-8 and Uio-66 (Figures S9 and S10, Supporting Information). 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 (Tables S5 and S7, Supporting Information). The difference between the terminal C=C and the secondary C=C is the molecular arrangement in the limited space (Figure S5, Supporting Information). 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.

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 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.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

metal nanoparticles, metal–organic frameworks, porous structure, site-selective catalysis, steric hindrance

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