

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- Title: Accelerating Selective Semihydrogenation by Metal-Organic Frameworks
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201913453 Angew. Chem. 10.1002/ange.201913453

Link to VoR: http://dx.doi.org/10.1002/anie.201913453 http://dx.doi.org/10.1002/ange.201913453

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Accelerating Selective Semihydrogenation by Metal-Organic Frameworks

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Abstract: Semihydrogenation of alkynes into alkenes against alkanes is of great importance in the chemical industries. Unfortunately, stateof-the-art heterogeneous catalysts hardly achieve high turnover frequency (TOF) simultaneously with near unity conversion, excellent selectivity and good stability. Here we demonstrate metal-organic frameworks (MOFs) containing Zr metal nodes (known as UiO) with tunable wettability and electron-withdrawing ability, which are easily realized by selecting organic linkers, as activity accelerators for semihydrogenation of alkynes catalyzed by the sandwiched palladium nanoparticles (Pd NPs). Impressively, the porous hydrophobic UiO supports not only enrich phenylacetylene (C₆H₅C≡CH) around Pd NPs but also endow Pd surfaces with less electrons, which leads to remarkable catalysis performance including exceptionally high TOF value of 13835 h⁻¹, 100% conversion of phenylacetylene, 93.1% selectivity toward styrene (C₆H₅CH=CH₂), and no activity decay after successive catalytic cycles. The strategy of molecularly-tailored supports is universal for boosting selective semihydrogenation of various terminal and internal alkynes.

Introduction

Beyond the conventional supported catalysts, the encapsulated structures of active noble metal NPs with the porous supports like molecular sieves^[1] and MOFs^[2] have been recognized as emerging heterogeneous catalysts. Such encapsulation not only maximizes the contact between active NPs and supports but also secures the NPs to prevent aggregation, so it has been widely utilized in different types of reactions to enhance the selectivity and stability of catalysts.^[2f,2g] Unfortunately, these encapsulated structures generally decrease the catalytic activity and the obtained TOF values are quite low, resulting from partial blockage of the transfer and diffusion of substrates and products.^[3,4]

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Supporting information for this article is given via a link at the end of the document. must be developed for accelerating catalytic reactions and breaking the trade-off between high conversion and good selectivity/stability.

A typical and critical example is selective semihydrogenation of alkynes, which is an extremely important and valuable transformation owing to broad application of the target products (alkenes) in pharmaceuticals, vitamins, agrochemicals, fragrances, polymerization and olefin metathesis reactions, etc.^{[5,} ^{6]} To find the hydrogenation catalysts of high selectivity always remains great challenge, since the adsorption capability of C=C and C=C groups over active metal sites is very difficult to be distinguished and accordingly the overhydrogenation products (alkanes) are hardly avoided. Many supports including CaCO₃,^{[7,} ^{8]} metal oxides,^[4,5g,9,10] carbon materials,^[11] molecular sieves^[12] and MOFs^[13] have been utilized for enhancing the selectivity^[5c] but the reported catalysts show rather low TOF values.

In this work, we choose MOFs, which are formed by selfassembly of metal ions or clusters with ditopic or polytopic organic linkers, as the porous encapsulation supports due to their advantages including abundant composition, large surface area and ordered pore structure.[14-16] Indeed, MOFs have exhibited great potential in catalytic liquid phase reactions, for example, some strategies have been developed to improve the catalytic performance by functionalizing the organic linker of MOFs with different functional group.^[17] In addition. Pd NPs are employed as the active components because of their moderate reactivity to H_2 and stronger adsorption of C=C group than C=C group compared with other noble metal NPs such as Pt, Au or Ag,^[18] which might alleviate overhydrogenation of alkynes to some extent. We show that the organic linkers in MOFs supports, which receive much less attention in catalytic reactions compared with metal nodes, are the key to accelerate semihydrogenation of multiple alkynes to alkenes.

Results and Discussion

To achieve highly efficient semihydrogenation reaction, we suggest that Pd NPs are sandwiched by UiO core and shell (UiO = University of Oslo) with different pore aperture and wettability via extension of the frameworks from terephthalic acid (H₂BDC) to 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂BPYDC), biphenyldicarboxylic acid (H₂BPDC) and diterephthalic acid (H₂TPDC),^[15] termed as UiO-66, UiO-67(N), UiO-67 and UiO-68, respectively (Figure 1a and 1b). The micro-sized UiO-67, which is synthesized by reacting Zr⁴⁺ ion with H₂BPDC, is chosen as the standard core to fabricate the sandwich-like UiO-67@Pd@UiO-X (X = 66, 67(N), 67 and 68) composites with identical morphology and shell thickness. The specific surface areas of pure MOFs

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microcrystals are 915 m² g⁻¹ for UiO-66, 2456 m² g⁻¹ for UiO-67(N), 2409 m² g⁻¹ for UiO-67 and 2061 m² g⁻¹ for UiO-68, while the average pore sizes are 0.85 and 1.18 nm for UiO-66, 1.10 nm for UiO-67, 1.10 nm for UiO-67(N), 1.71 and 2.36 nm for UiO-68 (Figures 1c, S1-S4 and Table S1),^[15,19] exemplifying their tunable pore structures. More importantly, the wettability property of UiOs is also modulated by changing their backbones. Density functional theory (DFT) calculation was performed to assess the wettability property of UiOs (Figure S5).[20] With increasing the number of benzene rings in H₂BDC, H₂BPDC and H₂TPDC, the calculated oil-water partition coefficient (logPoctanol/water) is -33.27, -15.94 and 1.33, revealing that the hydrophobicity of UiOs is obviously increased via extension of their backbones with more benzene rings (Table S2). Note that owing to the presence of pyridylazo in H₂BPYDC, UiO-67(N) is more hydrophilic than UiO-67 and the corresponding logPoctanol/water value is -330.23. The order of theoretical calculation is verified by contact angle experiment: 34.1° for UiO-67(N) < 41.2° for UiO-66 < 74.3° for UiO-67 < 90.5° for UiO-68 (Figure 1d). The molecularly-tunable pore size and wettability property of MOF supports offer the foundation for high activity catalysis.



Figure 1. Pd NPs sandwiched by UiO core and shell with different pore aperture and wettability, UiO-67@Pd@UiO-X (X = 66, 67(N), 67 and 68). a) Synthesis route. b) Structure units of different UiOs via extension of their frameworks from H₂BDC to H₂BPYDC, H₂BPDC and H₂TPDC. c) Pore size distributions of UiO-66, UiO-67(N), UiO-67 and UiO-68. d) Contact angles of UiO-66, UiO-67(N), UiO-67 and UiO-68 measured by water adsorption technique at 25°C.

Among the sandwich-like catalysts mentioned above, the UiO-67@Pd@UiO-67 is used as a representative for preparation process and structure analysis. In brief, UiO-67 core was synthesized by coordinating Zr^{4+} ions with H₂BPDC in the N,Ndimethylformamide (DMF) solution via a solvothermal method.^[15,21] As-obtained products are of uniformly octahedral shape with a mean diameter of 2.8 µm, and their crystal structure is indexed to the cubic phase (Figure S3). Subsequently, UiO-67 was impregnated with the aqueous metal precursor, H₂PdCl₄, to form a homogeneous solution. The reducing agent, NaBH₄, was then added into the above solution drop by drop to produce UiO-67@Pd samples characteristic of Pd NPs of ~3.5 nm in diameter uniformly dispersed on the surface of UiO-67 rather than inside the pore, which was mainly ascribed to the hydrophobic nature of UiO-67 and low Pd loading (Figures S6 and S7). Finally, the sandwich-like UiO-67@Pd@UiO-67 composites were fabricated by coating with UiO-67 shells (Figure 2), which were well dispersed in the organic solvents such as DMF and ethylacetate (Figure S8).

Transmission electron microscopy (TEM) images show that the obtained sandwich-like structures inherit the octahedral shape of UiO-67 core, and the average shell thickness is, respectively, controlled to be 35 and 50 nm via optimizing the precursor concentration and coating time, which is denoted as UiO-67@Pd@UiO-67 (35 nm) and UiO-67@Pd@UiO-67 (50 nm) (Figures 2a-2d, S9 and S10). Powder X-ray diffraction (XRD) patterns of UiO-67@Pd@UiO-67 (35 nm) and UiO-67@Pd@UiO-67 (50 nm) display only one set of peaks corresponding to crystalline UiO-67 (Figure 2e), and the absence of characteristic XRD peaks of Pd NPs is ascribed to their small size and low content (0.66% and 0.59% by weight. Table S3). As comparison. the exposed (111) facets of Pd NPs can be clearly discerned by high-resolution TEM imaging (Figure 2f). High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) of the cross-section of UiO-67@Pd@UiO-67 (50 nm) clearly indicates that a layer of Pd NPs are uniformly distributed between the UiO-67 core and shell (Figure 2g and 2h).



Figure 2. Morphology of sandwich-like UiO-67@Pd@UiO-67 structures. a, b) TEM images of UiO-67@Pd@UiO-67 (35 nm). c, d) TEM images of UiO-67@Pd@UiO-67 (50 nm). e) XRD patterns of UiO-67@Pd@UiO-67 (35 nm) and UiO-67@Pd@UiO-67 (50 nm). f) HRTEM image of Pd NPs inside UiO-67 matrix in a). g) HAADF-STEM mapping images of the cross-section of UiO-67@Pd@UiO-67 (50 nm), and h) magnification of the part marked with red rectangle in g).

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Noteworthily, we have found that UiO-67@Pd is a universal core platform that might be coated with other UiO shells including UiO-66, UiO-67(N) and UiO-68. The shell thickness is controlled to be almost same, and the corresponding shell thickness is 44 nm for UiO-66, 50 nm for UiO-67(N), and 48 nm for UiO-68 in sequence (Figures S11-S13). As-achieved composites are named as UiO-67@Pd@UiO-66 (44 nm), UiO-67@Pd@UiO-67(N) (50 nm) and UiO-67@Pd@UiO-68 (48 nm), respectively.

The catalytic performance of different UiO-67@Pd@UiO-X (X = 66, 67 and 68) samples is firstly evaluated based on selective semihydrogenation of PA (9.98 × 6.69 Å) toward styrene (ST) against ethyl benzene (EB). The typical contrast samples including pure Pd NPs, carbon sphere@Pd and UiO@Pd samples are also tested (Figures S6, S14-S18). The average size of Pd NPs is 8.8 nm for pure Pd NPs, 3.2 nm for carbon sphere@Pd, 5.0 nm for UiO-66@Pd, 3.5 nm for UiO-67@Pd and 4.5 nm for UiO-68@Pd. All the samples mainly expose the (111) facets of Pd NPs. To make the performance evaluation more comparable, the absolute amount of active Pd NPs in each sample is controlled to be the same (~0.015 mg, Table S3) and the PA to Pd molar ratio is 6456.

Table 1 summarizes the catalytic results, in which symbol A, B and C in the first row represent reactant alkynes, target product alkenes and byproduct alkanes, respectively (Table S4). No hydrogenation of PA catalyzed by pure UiO is found (Table 1, entry 10), while pure Pd NPs in size of 8.8 nm exhibit the conversion of 100% within 195 min reaction and the corresponding selectivity of target ST is 81.8% with a TOF value of 1987 h⁻¹ (Table 1, entry 9, Figure S19). When we used carbon sphere@Pd sample with Pd NPs of 3.2 nm in diameter as catalyst, the conversion of 100% and the selectivity of 86.8% with a TOF value of 3689 h⁻¹ are obtained (Table 1, entry 8, Figure S20). The higher catalytic activity is mainly caused by the smaller sized Pd NPs (3.2 nm) in carbon sphere@Pd sample compared with pure Pd samples (8.8 nm). With respect to bare Pd NPs and carbon sphere@Pd samples, the supported UiO@Pd samples display the significantly enhanced catalytic efficiency. UiO-66@Pd sample shows the conversion of 100% and the selectivity of 89.1% with a TOF value of 12912 h⁻¹ (Table 1, entry 5, Figure S21), UiO-67@Pd sample exhibits the conversion of 100% and selectivity of 88.1% with a TOF value of 19368 h⁻¹ (Table 1, entry 6, Figure S22), and UiO-68@Pd sample manifests the conversion of 100% and selectivity of 87.4% with a TOF value of 29798 h⁻¹ (Table 1, entry 7, Figure S23). Evidently, the TOF value is gradually increased by introducing more benzene rings in the linear dicarboxylates, which gives rise to the improved hydrophobicity of UiOs and causes enrichment of more organic substrate PA around Pd NPs for hydrogenation reaction.

Based on the above results from the contrast experiments, UiO-67@Pd@UiO-X (X = 66, 67 and 68) samples characteristic of shells with varied pore aperture and wettability are adopted as catalysts for selective semihydrogenation of PA. UiO-67@Pd@UiO-66 (44 nm) shows the conversion of 100% and the selectivity of 91.1% with a very small TOF value of 775 h⁻¹ (Table 1, entry 1, Figure S24). The low activity originates from the small pore aperture of UiO-66 shell that blocks mass transfer of both PA and ST during the catalytic process. This deduction is verified by **Table 1.** Selective semihydrogenation of different alkynes into alkenes by using various catalysts of this work.^a The detailed comparison with relevant literature works is aummarized in Table S8, and the result in this work is superior to all the reported heterogeneous catalysts, displaying unprecedented activity and excellent selectivity.

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	Catalysts	t	Conv. ^b	Sel. ^b (%)		TOF℃	
Entry		(min)	A (%)	В	С	(h-1)	
Substra	ate I: phenylacetylene						
1	UiO-67@Pd@UiO-66 (44 nm)	500	100	91.1	8.9	775	
2	UiO-67@Pd@UiO-67 (35 nm)	25	100	92.0	8.0	15495	
3	UiO-67@Pd@UiO-67 (50 nm)	28	100	93.1	6.9	13835	
4	UiO-67@Pd@UiO-68 (48 nm)	22	100	88.6	11.4	17608	
5	UiO-66@Pd	30	100	89.1	10.9	12912	
6	UiO-67@Pd	20	100	88.1	11.9	19368	
7	UiO-68@Pd	13	100	87.4	12.6	29798	
8	Carbon sphere@Pd	105	100	86.8	13.2	3689	
9	Pd NPs	195	100	81.8	18.2	1987	
10	UiO-66, UiO-67 or UiO-68	180	-	-	-		
11	UiO-67@Pd@UiO-67(N)(50 nm)	380	100	83.1	16.9	1019	
12	UiO-67(N)@Pd@UiO- 67(N)(14 nm)	480	100	75.3	24.7	807	
13	UiO-67(N)@Pd	135	100	83.0	17.0	2869	
14	MOF-74(Ni)@Pd	125	100	88.2	11.8	3099	
Substra	ate II: 4-ethynyltoluene						
15	UiO-67@Pd@UiO-67 (50 nm)	38	100	89.2	10.8	10194	
Substra	ate III: cyclohexylethyne						
16	UiO-67@Pd@UiO-67 (50 nm)	32	100	89.6	10.4	12105	
Substra	ate IV: 1-octyne						1
17	UiO-67@Pd@UiO-67 (50 nm)	35	100	93.2	6.8	11068	
Substra	ate V: 4-pentyn-1-ol						
18	UiO-67@Pd@UiO-67 (50 nm)	30	100	90.6	9.4	12912	
Substra	ate VI: 2-methyl-3-butyn-2-ol						
19	UiO-67@Pd@UiO-67 (50 nm)	14	100	88.8	11.2	27669	
Substra	ate VII: 2-butyne						
20	UiO-67@Pd@UiO-67 (50 nm)	15	100	96.7	3.3	25825	
Substra	ate VIII: 3-hexyne						
21	LiO-67@Pd@LliO-67 (50 nm)	20	100	95.3	47	19368	

^a Reaction condition: each catalyst containing 0.015 mg Pd NPs, 0.91 mmol alkynes, alkyne to Pd molar ratio of 6456, 10°C and 0.5 MPa H₂. ^b Conversion of alkyne and selectivity of alkene were determined by gas chromatography. ^c TOF was calculated by the mole number of converted substrate (mole number of total Pd)⁻¹.h⁻¹.

dimension comparison that the molecule size of PA is 9.98×6.69 Å while the pore aperture of UiO-66 is around 7 Å.^[15] When UiO-67 and UiO-68 with bigger pore aperture (around 8 Å and 10 Å) and better hydrophobic property are employed as the shells, their catalytic performance is dramatically improved. UiO-67@Pd@UiO-67 (50 nm) sample displays the conversion of 100% and the selectivity of 93.1% with a TOF value of 13835 h⁻¹ (Table 1, entry 3, Figure S25 and Table S5), and UiO-67@Pd@UiO-68 (48 nm) sample exhibits the conversion of 100%

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and the selectivity of 88.6% with a TOF value of 17608 h⁻¹ (Table 1, entry 4, Figure S26). More importantly, the utilization of UiO-67 and UiO-68 shells results in improvement of the selectivity toward ST (93.1% for UiO-67@Pd@UiO-67 (50 nm) and 88.6% for UiO-67@Pd@UiO-68 (48 nm)), likely benefitting from the interface synergy effect between Pd NPs and porous UiO in the sandwich-like structure. We also find that the activity and selectivity of these sandwich-like catalysts are easily manipulated by altering the shell thickness, for instance, UiO-67@Pd@UiO-67 (35 nm) of thinner shell shows a larger TOF value of 15495 h⁻¹ but the slightly decreased selectivity of 92.0% (Table 1, entry 2, Figure S27). In short, the Pd NPs surrounded with the porous and hydrophobic MOFs exhibit the extremely high TOF values along with complete conversion and excellent selectivity in the semihydrogenation of PA.

To further investigate the semihydrogenation of PA under mild condition, the H₂ pressure is reduced from 0.5 MPa to the ambient pressure by bubbling hydrogen in the reaction solution. UiO-67@Pd@UiO-67 (50 nm) sample still exhibits the high selectivity of 97.4% to ST, but the conversion of PA is dramatically decreased to 17.6% at the reaction time of 28 min, indicating that semihydrogenation of PA prefers occurring at a higher H₂ pressure (Figure S28 and Table S6). In addition, due to the high surface area of sandwich catalysts, the physical adsorption of substrates and products needs to be considered. To evaluate the potential of sandwich UiO-67@Pd@UiO-67 (50 nm) as efficient catalyst, a higher PA to Pd molar ratio of 19368 is selected (Figure S29 and Table S7). The experimental result shows that at 18.5% conversion of PA, the selectivity of ST is 97.0% with the TOF value of 21499 h⁻¹, suggesting that UiO-67@Pd@UiO-67 (50 nm) catalyst exhibits the higher catalytic activity compared with the PA to Pd molar ratio of 6456. With extending the reaction time, the TOF value gradually decreases. When the conversion of PA reaches 100%, the selectivity of ST is 91.7% and corresponding TOF value is 9684 h⁻¹. It is noted that sandwich UiO-67@Pd@UiO-67 (50 nm) catalyst still possesses the excellent catalytic activity and selectivity of ST at a higher PA to Pd molar ratio.

Beside the activity and selectivity, stability is known to be another key parameter to evaluate the performance of catalysts. No obvious deactivation occurs on UiO-67@Pd@UiO-67 (50 nm) sample at the conversion of either 52.6% or 97.5% after five successive recycle tests, respectively, resulting from the firm immobilization of active Pd NPs inside the sandwich-like structures (Figure 3a, 3b, 3d and 3e). On the contrary, the conversion using the supported UiO-67@Pd is considerably decreased from 97.2% to 53.8% after five successive recycle tests. TEM images indicate severe aggregation of Pd NPs on the surface of UiO-67 (Figure 3c, 3f and 3g). These indicate that coating the supported catalyst with porous MOF shells is an effective way to achieve the heterogeneous catalysis with high stability.



Figure 3. Stability test of UiO-67 @Pd@UiO-67 (50 nm) along with UiO-67@Pd samples. Catalytic selective semihydrogenation of PA by UiO-67@Pd@UiO-67 (50 nm) for five successive runs at the conversion of a) 97.5% and b) 52.6%. c) Catalytic selective semihydrogenation of PA by UiO-67@Pd sample for five successive runs. d, e) TEM images of UiO-67@Pd@UiO-67 (50 nm) sample before and after catalytic reactions in a). f, g) TEM images of UiO-67@Pd sample before and after catalytic reactions in c).

To clarify the importance of shell wettability on the catalytic performance, more hydrophilic UiO-67(N) is selected (as evidenced in Figure 1d), and three samples including UiO-67(N)@Pd, UiO-67@Pd@UiO-67(N) (50 nm) and UiO-67(N)@Pd@UiO-67(N) (14 nm) are prepared (Figures S12, S30 and S31). The average sizes of Pd NPs are 3.0 nm for UiO-67(N)@Pd, 4.0 nm for UiO-67@Pd@UiO-67(N) (50 nm), and 3.4 nm for UiO-67(N)@Pd@UiO-67(N) (14 nm). When used as catalysts for selective semihydrogenation of PA, UiO-67(N)@Pd sample shows the conversion of 100% and the selectivity of 83.0% with a considerably low TOF value of 2869 h⁻¹ (Table 1, entry 13, Figure S32), demonstrating that the hydrophilic supports are unfavorable for hydrogenation of PA. As for the sandwich-like UiO-67@Pd@UiO-67(N) (50 nm) and UiO-67(N)@Pd@UiO-67(N) (14 nm) samples, the TOF value is only 1019 h⁻¹ and 807 h⁻¹ (Table 1, entries 11 and 12, Figures S33 and S34), respectively. In addition, the Pd NPs supported by UiO-67(N) sample show the dramatic decrease in the selectivity toward ST. e. a. 75.3% for UiO-67(N)@Pd@UiO-67(N) (14 nm) vs. 93.1% for UiO-67@Pd@UiO-67 (50 nm) (Table 1, entries 3 and 12). As for the decreased activity, it is mainly caused by the hydrophilic property of UiO-67(N); while in regard of the decreased selectivity, it is associated with the electronic structure of active Pd NPs modulated by UiO-67(N) as will be discussed below.

For performance comparison, we also summarize the outstanding results from recent literature works (Table S8). Superior to all the reported heterogeneous catalysts, semihydrogenation of PA on UiO-67@Pd@UiO-67 (50 nm) displays the extraordinary activity, excellent selectivity and good stability.

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Figure 4. XPS profiles of UiO-67@Pd and UiO-67(N)@Pd samples along with UiO-67, UiO-67(N) and pure Pd NPs. a) Pd 3*d* level for pure Pd NPs and UiO-67@Pd. b) Zr 3*d* level and c) O 1s level for pure UiO-67 and UiO-67@Pd. d) Pd 3*d* level for pure Pd NPs and UiO-67(N)@Pd. e) N 1s level and f) O 1s level for pure UiO-67(N) and UiO-67(N)@Pd. Inserted numbers represent the peak positions of different elements.

X-ray photoelectron spectroscopy (XPS) was performed to inspect the interfacial interaction between Pd NPs and UiO supports. As for pure Pd NPs, characteristic Pd 3d_{5/2} binding energy at 335.66 eV is assigned to zero-valent Pd in the metallic state.^[22] With respect to UiO-67@Pd sample, Pd 3d_{5/2} binding energy shifts toward a higher value of 335.93 eV, and the corresponding binding energy of Zr 3d_{5/2} shifts toward a lower value of 182.74 eV compared with that of pure UiO-67 sample (Figure 4a and 4b, and Figure S35a). Similarly, Pd 3d_{5/2} binding energy of UiO-66@Pd and UiO-68@Pd shifts toward higher value of 336.06 eV and 335.86 eV, and the corresponding binding energy of Zr 3d_{5/2} shifts toward lower value of 182.81 eV and 182.96 eV compared with pure UiO-66 and UiO-68, respectively (Figures S36 and S37). These suggest that there is electron transfer from Pd NPs to UiO-66, UiO-67 or UiO-68. Moreover, O 1s binding energy shifts toward a lower value for UiO-67@Pd with respect to that in pure UiO counterparts due to the strong interfacial interaction between Pd NPs and Zr nodes in UiO-67 (Figure 4c, and Figure S38a).^[23]

In sharp contrast, Pd $3d_{5/2}$ binding energy of UiO-67(N)@Pd sample shifts to a lower value of 334.60 eV compared with pure Pd NPs (Figure S35b), while the corresponding binding energy of

N 1s shifts to a higher value of 399.76 eV with respect to pure UiO-67(N) (Figure 4d-4f). The interfacial electron transfer from UiO-67(N) to Pd NPs occurs in UiO-67(N)@Pd, because the lonepair electrons of N in UiO-67(N) frameworks prefer moving to lowlying bonding states (Figure S38b). Altogether, the electronic structure of Pd NPs could be effectively manipulated by grafting different functional organic linkers into UiO frameworks.

To elucidate the effect of electronic structure of Pd NPs on the selectivity of ST, DFT calculations were done on the neutral and charged Pd(111) surfaces, which present the most exposed facets of Pd NPs (Figure 2f), using a four-layered (3 × 3) supercell composed of 36 Pd atoms (see the detailed calculation method in the Supporting Information). The most stable adsorption of H₂, PA, ST and EB on the neutral Pd(111) surface is compared. H₂ adsorbs on the neutral Pd surface in a dissociation mode and H atom prefers attaching at the hollow site with an adsorption energy of -2.63 eV (Figure S39a). The aromatic rings of adsorbates are strongly bonded to the Pd surface with a distance of 2.3 Å, while the H atoms on benzene rings lift away from the surface, which makes C-H bonds a hybridization transition from sp^2 to sp^3 (Figure S39b). Interestingly enough, the alkynyl group of PA and the alkenvl group of ST exhibit different adsorption configuration on the Pd surface. The alkynyl group of PA is bonded tightly to the Pd surface with a distance of 2.1 Å, which is even closer than that of the aromatic ring to the surface; meanwhile, the hydrogen atom of the alkynyl group is 50° away from the surface, suggesting the C-H hybridization transition from sp to sp². As for semihydrogenation product ST (Figure S39c), the distance between the alkenyl group of the ST and Pd surface is 2.2 Å, more away from the surface than the alkynyl group of PA, implying that weaker bonding of the alkenyl group than the alkynyl group on the Pd surface. When ST is hydrogenated to EB, the alkyl group has no interaction with the Pd surface, suggesting its facile desorption (Figure S39d).

The reaction pathway is calculated to understand the selective semihydrogenation of PA to ST (Figures 5 and S40). As plotted, PA firstly adsorbs on Pd(111) surface to form the adsorbed state (named as PA*) and then converts to ST*, followed by competitive process of its desorption or hydrogenation to EB*. Clearly, the key for enhancing the selectivity of ST is to promote desorption of ST* against its hydrogenation on the Pd surface. With respect to neutral Pd(111) surface, PA* is stabilized with an adsorption energy of -1.64 eV, and then is converted to ST* with an exothermicity of -1.34 eV. Subsequently, desorption of ST* is endothermic by 1.49 eV, whereas hydrogenation of ST* to EB* is an exothermic process that needs to overcome two energy barriers of 0.55 eV for transition state (TS1) of forming PhCHCH3* and 1.12 eV for transition state (TS2) of forming PhCH₂CH₃*. Thus, the energy cost on desorption of ST^\ast and hydrogenation of ST^\ast to EB* is comparable on the neutral Pd(111) surface. As for Pd(111) surface with a positive charge of 0.6 in UiO-67@Pd samples, the adsorbates show weak adsorption, and the desorption energy of ST* is only 0.33 eV, which is much lower than the energy barriers of TS1 (0.55 eV) and TS2 (1.12 eV) for hydrogenation of ST* to EB* on neutral Pd(111) surface. Evidently, ST* prefers desorbing on the positive Pd surface, and correspondingly the selectivity of ST product is enhanced. As comparison, the desorption energy of ST* (2.24 eV) on the Pd(111) surface with a negative charge of 0.6 in UiO-67(N)@Pd samples is greatly higher than energy

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barriers of TS1 (0.55 eV) and TS2 (1.12 eV) for hydrogenation of ST^{*} to EB^{*} on neutral Pd(111) surface, thus leading to decrease in selectivity of ST.



Figure 5. Potential energy profiles of hydrogenation of PA on Pd(111) by using the (3 × 3) supercell composed of 36 Pd atoms. a) PhCCH*, b) PhCHCH₂*, c) TS1, d) PhCHCH₃*, e) TS2, f) PhCH₂CH₃*. Black, red and blue short lines stand for the neutral, positive ($\overline{\delta}$ = + 0.6) and negative ($\overline{\delta}$ = - 0.6) Pd(111) surfaces in turn. The values refer to the experimental temperature (T = 283.15 K).

All the above results disclose that the positive Pd(111) surface in UiO-67@Pd samples, which are caused by interfacial electron transfer from Pd NPs and UiO supports, contributes to highly selective formation of ST rather than EB. To further validate this deduction, the interfacial electron transfer between Pd(111) and PA/ST is firstly analyzed. Bader charge analysis discloses that the electron transfer is from neutral Pd (111) surfaces to PA and ST in the adsorption structures, and correspondingly, the calculated electron transfer value is 0.43 e for Pd to PA and 0.29 e for Pd to ST (Figure S41). Then, the charges on the Pd surface ranging from -0.6 to 0.6 are systematically calculated for the adsorption/desorption of PA and ST (Figure S42). With increase in the negative charge on Pd(111) surface, the adsorption of PA and ST becomes stronger; whereas it turns weaker with increase in the positive charge, meaning that the higher selectivity of ST is obtained. This analysis is consistent with recent observation about the adsorption of PA and ST on the surfaces of Ni-O(111) and Ni(111).^[24] Note that that the order for selectivity of ST on different UiO@Pd samples follows UiO-66@Pd (Sel.: 89.1%) > UiO-67@Pd (Sel.: 88.1%) > UiO-68@Pd (Sel.: 87.4%) (Table 1, entries 5-7), which is in good agreement with the binding energy shift order from Pd to UiO with respect to pure Pd NPs, i.e. 0.4 eV for UiO-66@Pd > 0.27 eV for UiO-67@Pd > 0.2 eV for UiO-68@Pd (Figures 4, S36 and S37).

To further distinguish the key factors influencing catalytic activity and selectivity, an electron-withdrawing but hydrophilic MOF-74 (contact angle of 24°),^[2e] which is formed via coordination of Ni²⁺ ion with 2,5-dihydroxyterephthalic acid and characteristic with pore size of 1.47 nm, is selected as the support (Figures S43-S45). The average size of Pd NPs in as-synthesized MOF-74@Pd is 4.4 nm. When MOF-74@Pd is used as hydrogenation catalyst, the conversion of PA and selectivity of ST are 100% and 88.2% with a TOF value of 3099 h⁻¹ (Table 1, entry 14, Figure S46). With respect to UiO-67@Pd, MOF-74@Pd displays much lower TOF value (3099 h⁻¹ vs. 19368 h⁻¹) but identical selectivity

(88.2% vs. 88.1%), ascribing to wettability mismatch between hydrophilic MOF-74 pores and hydrophobic substrates. Moreover, compared with UiO-67(N)@Pd, MOF-74@Pd shows similar TOF value (3099 h⁻¹ vs. 2869 h⁻¹) but considerably enhanced selectivity (88.2% vs. 83.0%), attributing to interfacial electron transfer from Pd NPs and MOF-74 supports (Figure S45). These results validate the experimental observations on catalytic performance of UiO-67@Pd@UiO-X toward selective semihydrogenation of PA (Table 1).

Other common terminal alkynes including 4-ethynyltoluene $(10.84 \times 6.69 \text{ Å})$, cyclohexylethyne $(9.98 \times 6.72 \text{ Å})$ and 1-octyne $(11.63 \times 5.03 \text{ Å})$ are employed as substrates for selective semihydrogenation reactions on UiO-67@Pd@UiO-67 (50 nm) (Figure S47). Remarkably, when the conversion is 100% for 4ethynyltoluene, cyclohexylethyne and 1-octyne, respectively, the corresponding selectivity is 89.2% for 4-methylstyrene with a TOF value of 10194 h⁻¹, 89.6% for cyclohexylethene with a TOF value of 12105 h⁻¹, and 93.2% for 1-octene with a TOF value of 11068 h⁻¹ (Table 1, entries 15-17, Figures S48-S50). When two typical alkynols including 4-pentyn-1-ol (8.89 x 4.80 Å) and 2-methyl-3butyn-2-ol (7.74 × 6.71 Å) are used as substrates and completely converted, the corresponding selectivity is 90.6% for 4-penten-1ol with a TOF value of 12912 h⁻¹, and 88.8% for 2-methyl-3-buten-2-ol with a TOF value of 27669 h⁻¹ (Table 1, entries 18 and 19, Figures S51 and S52). Last but not least, when two internal alkynes including 2-butyne (7.31 × 4.17 Å) and 3-hexyne (10.40 × 5.03 Å) are utilized as substrates and completely converted, the corresponding selectivity is 96.7% for 2-butylene with a TOF value of 25825 h⁻¹, and 95.3% for 3-hexene with a TOF value of 19368 h⁻¹ (Table 1, entries 20 and 21, Figures S53 and S54). Again, Pd NPs encapsulated by hydrophobic UiO shells show the unprecedented catalytic performances in semihydrogenation of different alkynes compared with the reported heterogeneous catalysts (Table S8).

Conclusion

In summary, semihydrogenation of different alkynes to alkenes is greatly accelerated via decoupling the functions of porous MOF supports at the molecular level. The hydrophobic UiO supports. via the incorporation of more benzene rings into the organic linkers, facilitate the enrichment of the organic alkynes around the active Pd NPs so as to promote the activity, while the electron transfer from Pd NPs to the electron-withdrawing UiO nodes leads to the weak adsorption of target alkene products over Pd NPs and consequently the enhanced selectivity. Thus, the unprecedented catalytic performances on selective semihydrogenation of multiple alkynes are acquired with UiO-67@Pd@UiO-67 (50 nm) sample, superior to all the reported heterogeneous catalysts (Table S8). The concept of on-demand molecular architecture of the supports will offer new venues for designing high-performance heterogeneous catalysts toward high value-added but challenging reactions.

Acknowledgements

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This work was supported financially by National Key Basic China Research Program of (2014CB931801 and 2016YFA0200700, Z.Y.T.), National Natural Science Foundation of China (21721002, 21475029 and 91427302, Z.Y.T.; 21722102, 51672053 and 21303029, G.D.L.), Beijing Natural Science Foundation (2182087, G.D.L.), Frontier Science Key Project of Chinese Academy of Sciences (QYZDJ-SSW-SLH038, Z.Y.T.), CAS-CSIRO Cooperative Research Program (GJHZ1503, Z.Y.T.), "Strategic Priority Research Program" of the Chinese Academy of Sciences (XDA09040100, Z.Y.T.), the project of "K.C. Wong Education Foundation" (Z.Y.T.), and Youth Innovation Promotion Association CAS (2016036, G.D.L.). We thank Dr. Peng Xu for testing and ananlyzing the XPS data.

Keywords: alkynes • metal-organic frameworks • palladium nanoparticle • selective semihydrogenation • wettability

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Metal-organic frameworks (MOFs) containing Zr metal nodes (known as UiO) with tunable wettability and electron-withdrawing ability, which are easily realized by selecting organic linkers, are used as activity accelerators for semihydrogenation of alkynes catalyzed by the sandwiched palladium nanoparticles simultaneously with unity conversion, excellent selectivity and good stability.



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