Pd@Zn-MOF-74: Restricting a Guest Molecule by the Open-Metal Site in a Metal−Organic Framework for Selective Semihydrogenation

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S *Supporting Information*

ABSTRACT: In this work, we found that the open-metal site in a metal−organic framework (MOF) can be used to enhance such selectivity. Hydrogenation of phenyl-acetylene over such a catalyst enables ultrahigh styrene selectivity of 92% at full conversion with a turnover frequency of 98.1 h^{-1}. The origin of ultrahigh selectivity, as unveiled by density functional theory calculation, is due to a coordination interaction between the open Zn(II) site and the C≡C bond of phenylacetylene.

Selective hydrogenation from alkynes to alkene rather than overreduction to alkanes, or the so-called semihydrogenation, presents one of the most important industrial processes because of its irreplaceable application in the production of intermediates for fine chemicals and the purification of alkenes for the production of polyolefins.[1] For example, removing trace acetylene by means of selective semihydrogenation is the most welcome method in the ethylene industry[2] because the existence of trace acetylene in ethylene will not only significantly affect the quality of the resulting polyethylene but also block the fluid stream and, consequently, cause an explosion.

In principle, such semihydrogenation is a highly structure-sensitive reaction, and overhydrogenation is more thermody-namically favored if without suitable control.[3] To prevent such an undesired trend, Pd-based catalysts are most widely used; however, inherent overhydrogenation, thus leading to low selectivity, is often encountered at high conversion, especially full conversion.[4] For example, the commercial Pd/C catalyst shows poor selectivity at 100% conversion and no selectivity with increasing reaction time for semihydrogenation on phenylacetylene. To solve this drawback, in the literature, two distinct strategies have been established. One is the construction of Pd-based intermetallic compounds such as Pd−Ag, Pd−Au, Pd−Cu, Pd−In, and Pd−Ga, mainly dependent on their well-ordered structures.[5,6] Another method is modifying Pd NPs by harmful promoters such as Pb in the commonly used Lindlar, or recently reported organic ligands (NanoSelect).[7] Generally speaking, the support is also an important component to affect the final catalytic performance. However, we notice that there is still no report about the use of support as a decisive factor to render high selectivity. In this regard, our research focuses on the development of a metal−organic framework (MOF)-supported Pd catalyst for selective semihydrogenation, thus expecting to offer unrivaled opportunities for desired efficient catalytic transformation.

MOFs built on metal ions and various organic connectors present one of the most impressive porous materials.[8] During the past decades, we have witnessed the booming of such materials and a broad application covering gas storage, separation, catalysis, sensing, and so on.[9−11] In contrast to the traditional porous carbon and zeolite, MOFs own several outstanding merits such as diversity, myriad candidates available, designable structures, and uniform pores. Especially, the open-metal site in MOFs is highly attractive because it is capable of offering strong affinity toward desired molecules, thus leading to a superior performance in many fields that could not be achieved by the common method. For example, the open Cu(II) site in FJI-H8 reported by Yuan et al. enables strong Cu−acetylene interaction, thus creating a record-high gravimetric acetylene uptake.[12] The MOF-74 series as a CO_2/N_2 separation benchmark is mainly due to the open-metal sites that could coordinate with CO_2 rather than N_2.[13] In this regard, the open-metal site in MOFs can be viewed as a magic tool to fix molecules, especially structure-sensitive molecules, thus possibly offering the most unique selectivity for catalysis, as evidenced by the recent achievements reported by Tang et al.,[14] where the open-metal site in MOFs provides preferential interaction with the C=O group over the C=C group, leading to the selective hydrogenation of α,β-unsaturated aldehydes on the C=O group.

Moreover, following LaMer and Dinegar's concept,[15] the synthesis of monodisperse NPs must need a protecting agent such as poly(vinylpyrrolidone) (PVP) to balance the processes of particle nucleation and growth. Nevertheless, during the whole catalytic process, the protecting agent is undesired and must first be removed to release the surface of metal NPs. Accordingly, annealing, such as calcination, was carried out to remove the stabilizing agents, which, however, often leads to some unexpected effect on the NPs and thus seriously reduces its

catalytic performance.[16] Thereby, developing a protecting-agent-free strategy is highly desirable but extremely challenging because of its inherently synthetic difficulty.

Taking the above discussion into account, in this work we devote ourselves to exploiting a MOF-supported Pd catalyst for selective semihydrogenation. As shown in Scheme 1, Zn-MOF-

Scheme 1. Schematic Description of the Spray Strategy for Fabricating Pd NPs without PVP and a Zn-MOF-74 Support with an Open-Zn Site Providing Affinity toward the C≡C Bond of Phenylacetylene
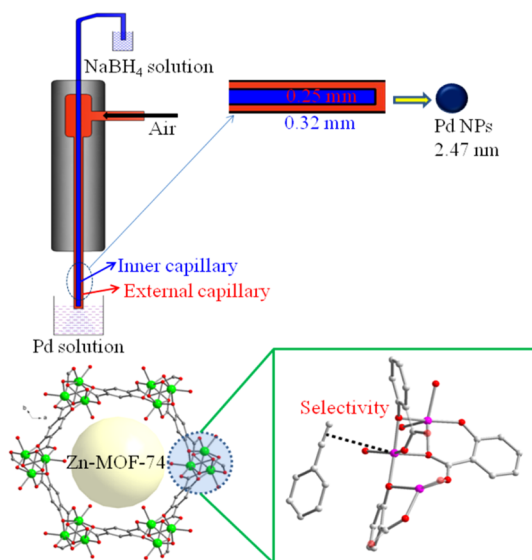
74 is selected as the support and is expected to endow selectivity because of coordination interaction between the C≡C bond of phenylacetylene and the open-Zn site. To avoid the use of PVP, a spray strategy is, for the first time, employed to generate Pd NPs.

The Pd@Zn-MOF-74 composite was synthesized as follows. First, the generation of Pd NPs was executed by the spray approach. As shown in Scheme 1, the homemade spray equipment is composed of two basic components, viz., inner and outer capillaries with sizes of 0.25 mm × 0.32 mm, which are used to deliver solution and air, respectively. The velocity of air was controlled by a flowmeter at 500 mL/min. The $Pd(NO_3)_2$ and $NaBH_4$ concentrations were 500 and 1130 ppm, respectively. To prevent the aggregation of generated Pd NPs, a $NaBH_4$ solution was used to produce the foglike droplet. A black Pd NP solution was obtained within 5 min, as shown in Figure 1. Anchoring Pd NPs on Zn-MOF-74 is achieved by adding 150 mg of Zn-MOF-74 crystals into the as-synthesized Pd NP solution and then stirring for 1 h.

The resulting composite of Pd@Zn-MOF-74 was initially characterized by transmission electron microscopy (TEM;
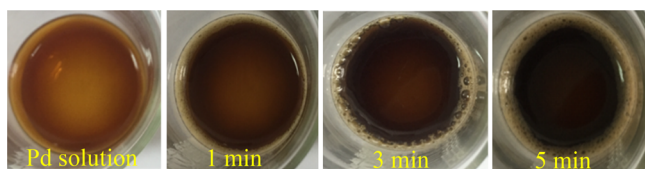

Figure 1. Photographs of the color change during the generation of Pd NPs in this work by using a spray strategy.

Figure 2a). Clearly, individual, uniform, and dispersed Pd NPs were observed as tiny dots on Zn-MOF-74. The average size of
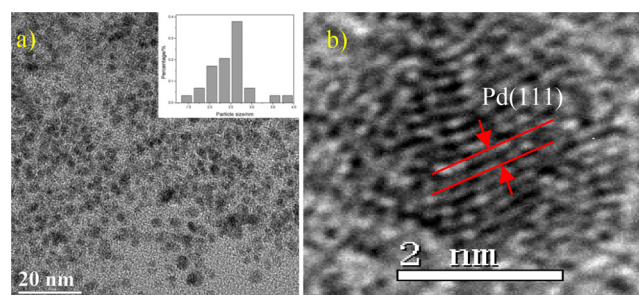
Figure 2. (a) TEM image of the Pd@Zn-MOF-74 composite and (b) HRTEM image of the Pd@Zn-MOF-74 composite. The inset is the corresponding distribution of the particle size. The highlighting indicates the Pd(111) lattice fingerprint.

Pd NPs was estimated to be 2.47 nm. Close examination by high-resolution TEM (HRTEM; Figure 2b) revealed that these Pd NPs displayed obvious lattice fringes of 0.23 nm from the Pd (111) plane, reflecting their high crystallinity.[4−7] The Pd content of 1.8 wt % was determined by inductively coupled plasma mass spectroscopy. The surface oxidation states of the Pd NPs were analyzed by Pd 3d core-level high-resolution X-ray photoelectron spectroscopy (HRXPS) via fitting with spin−orbit split $4f_{7/2}$ and $4f_{5/2}$ components (Figure 3). The
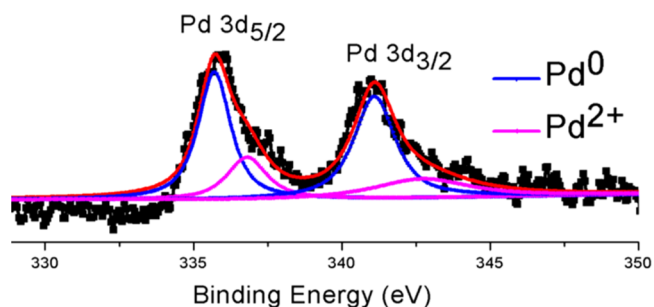
Figure 3. Pd HRXPS data of Pd@Zn-MOF-74 samples.

dominating oxidation state is metallic Pd with a typical $3d_{5/2}$ peak at 335.7 eV, while divalent Pd with a typical $3d_{5/2}$ peak at 336.9 eV is also observed.[4−7] The formation of divalent Pd on the surface of Pd NPs presumably stemmed from the superficial oxidation of Pd due to their nanosized feature.[4−7] Moreover, by comparing the powder X-ray diffraction (Figure S2) patterns among these samples involving as-synthesized Zn-MOF-74 and Pd@Zn-MOF-74, we found that the anchoring Pd NPs on Zn-MOF-74 do not affect the crystallinity and structure of Zn-MOF-74, and the peaks belonging to Pd NPs can be also detected.[4−7] Furthermore, we also carried out N_2 adsorption at 77 K for both Zn-MOF-74 and Pd@Zn-MOF-74 and found that the loading of Pd onto Zn-MOF-74 does not affect their apertures but significantly reduces their Brunauer−Emmett−Teller ET surface areas (Figure S3).

To confirm the catalytic performance for the resulting Pd catalyst, a hydrogenation reaction on phenylacetylene as a representative example was explored. The conversion and styrene selectivity are shown in Figure 4, and the catalytic performance of our MOF-supported Pd catalyst is also compared with that of the commercial (benchmark) Pd/C
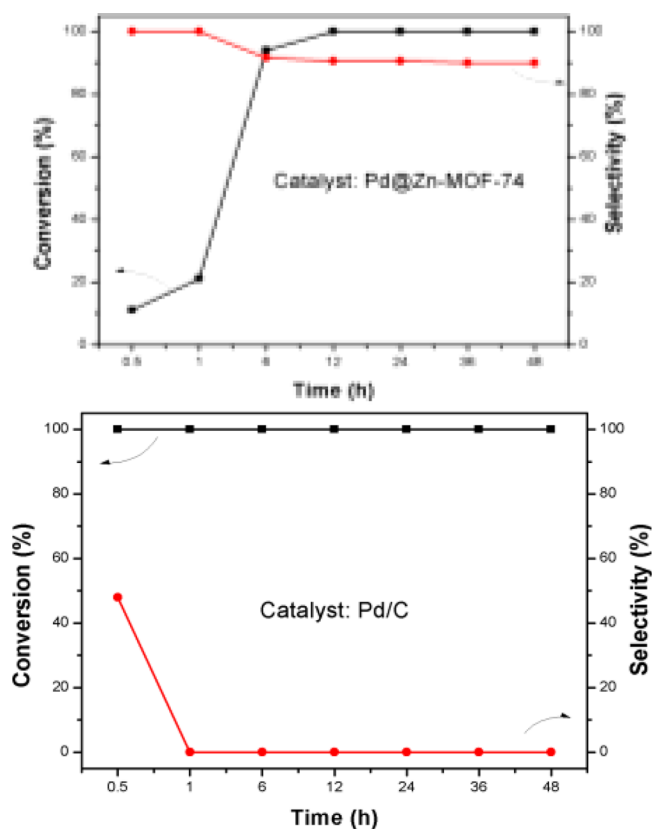
Figure 4. Hydrogenation of phenylacetylene over the Pd@Zn-MOF-74 catalyst and commercial (benchmark) Pd/C catalyst: (■) conversion of phenylacetylene; (●) desired styrene selectivity. Reaction conditions: phenylacetylene (1 mmol), hexane (15 mL), H_2 (1 bar, 40 °C), catalysts (5 mg).

catalyst. Remarkably, as shown in Figure 3a, the Pd@Zn-MOF-74 catalyst shows an ultrahigh styrene selectivity of 92% at full conversion within 12 h. A comparison with other reported catalysts for such issues is given in Table S1, clearly suggesting that our catalyst presents a highly rare example showing a high selectivity for semihydrogenation just based on a single Pd metal. The catalytic efficiency is evaluated by the turnover frequency value, giving 98.1 h^{-1}, suggesting a good catalytic efficiency. For a benchmark Pd/C catalyst, a lower selectivity of 48% at full conversion was observed at 0.5 h. After the reaction was prolonged to 48 h, we found that the selectivity for the Pd/C catalyst was rapidly decreased to 0% within 1 h. Impressively, almost no decrease in selectivity after 48 h was observed for the Pd@Zn-MOF-74 catalyst, which suggests that such a catalyst shows good resistance toward the formation of β-hydrides, which is inherently responsible for the poor selectivity for the Pd catalyst.[4] To confirm its workability, the hydrogenation reaction on another alkyne substrate of propiolic acid was carried out, and we found a similar excellent selective hydrogenation with 81% selectivity at 100% conversion (Figure S4). The recycle use of the Pd@Zn-MOF-74 catalyst is also confirmed, and we found that the recycle use enables a 95% selectivity at 100% conversion (Figure S5). Moreover, in the residual solution after the catalytic reaction, no detectable Pd can be observed, excluding the possibility of leaching of Pd from Pd@Zn-MOF-74 during the catalytic reaction.

The exceptional catalytic performance observed in the Pd@Zn-MOF-74 catalyst suggests that the Zn-MOF-74 support may

be a crucial factor to execute the selectivity because it is generally believed that a Pd catalyst without any modification by the established method enables poor selectivity,[4−7] as evidenced in a commercial (benchmark) Pd/C catalyst. To obtain a fundamental understanding of the present observation, a denstiy functional theory (DFT) calculation was carried out (Figure S7). In the phenylacetylene-loaded optimal structure, we found that the open-Zn site in Zn-MOF-74 serves as an active site to interact with the C≡C bond of phenylacetylene, giving a distance and a binding energy of 3.82 Å and −0.43 eV, indicative of thermodynamically favored binding. The calculated reaction energies for the hydrogenation of phenylacetylene to styrene or ethylbenzene are −2.53 and −1.05 eV, respectively, indicating that both semihydrogenation and overhydrogenation are all-exothermic and thus thermodynamically favored. However, the formation of styrene is obviously energetically favored over that of ethylbenzene, thus leading to a superior catalytic performance of 92% selectivity at 100% conversion for the present catalyst. To further confirm this claim, a comparison test based on the catalysts of Pd@Uio-66 and Pd@Uio-67 without an open-metal site was carried out, and we found that such a catalyst shows weak selectivity at 100% conversion for the hydrogenation reaction on phenylacetylene (0% for Pd@Uio-66 and 47% for Pd@Uio-67; Figure S7). Moreover, a catalytic reaction based on the $Zn(NO_3)_2$ source was also researched, and no catalytic activity was observed. Note that, in the IR spectrum, the character peak at 3400 cm^{-1} belonging to the C≡C bond of phenylacetylene was observed for the phenylacetylene-loaded Zn-MOF-74 sample, while the red shift to 583 cm^{-1} in phenylacetylene@Zn-MOF-74, relative to 577 cm^{-1} in Zn-MOF-74, was due to coordination between the C≡C bond of phenylacetylene and the open-metal site (Figure S8).

In conclusion, the finding in this work presents a highly rare case in the field of a noble-metal catalyst by using a MOF material to implement selective catalysis, opening up a gate based on a support strategy for semihydrogenation or other selective catalysis.

■ ASSOCIATED CONTENT

ⓈSupporting Information

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Material involved in synthesis and additional figures (PDF)

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