Metal–Organic Framework Composites

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Polydimethylsiloxane Coating for a Palladium/MOF Composite: Highly Improved Catalytic Performance by Surface Hydrophobization

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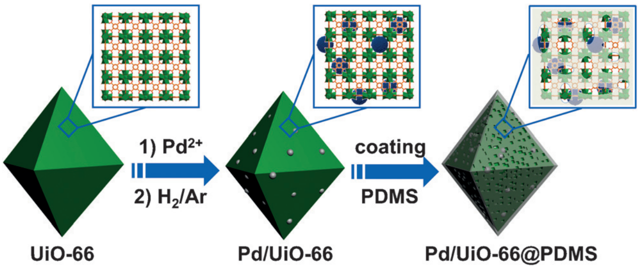
Abstract: *Surface wettability of active sites plays a crucial role in the activity and selectivity of catalysts. This report describes modification of surface hydrophobicity of Pd/UiO-66, a composite comprising a metal–organic framework (MOF) and stabilized palladium nanoparticles (NPs), using a simple polydimethylsiloxane (PDMS) coating. The modified catalyst demonstrated significantly improved catalytic efficiency. The approach can be extended to various Pd nanoparticulate catalysts for enhanced activity in reactions involving hydrophobic reactants, as the hydrophobic surface facilitates the enrichment of hydrophobic substrates around the catalytic site. PDMS encapsulation of Pd NPs prevents aggregation of NPs and thus results in superior catalytic recyclability. Additionally, PDMS coating is applicable to a diverse range of catalysts, endowing them with additional selectivity in sieving reactants with different wettability.*

The wettability control of a catalyst surface is widely known to be of great importance in the regulation of interactions between heterogeneous catalysts and reactants, which is directly related to catalytic activity and selectivity.[1] Hydrophilic or hydrophobic catalyst surfaces have particular affinity for the corresponding substrates, with beneficial consequences for catalytic conversion. For example, hydrophobic solid acid or base catalysts present high activity in various reactions involving hydrophobic reactants, such as epoxidation, hydrogenation, condensation, and esterification or *trans*-esterification reactions.[1a–e] Moreover, metal nanoparticles (NPs), which are highly active in a variety of reactions but readily agglomerated, can be stabilized by different porous materials. In such circumstances, hydrophobic modification of the pore surface can boost catalytic performance.[1f–h]

Emerging as a relatively new class of porous materials, metal–organic frameworks (MOFs) have captured wide research interest in recent years because of their crystalline nature, tailorable structures, and most importantly, multifunctional applications in diverse fields.[2–5] Among these, MOFs are recognized to possess the advantages of both homogeneous and heterogeneous catalysts and are thus very suitable for catalysis.[5] Moreover, high surface area and porosity make MOFs excellent supports or hosts for catalytically active metal NPs. There have been quite a few reports on metal NPs@MOF in recent years, almost all of which are focused on the confinement or stabilization of tiny metal NPs by MOFs for catalytic purposes.[6] Investigations on the effect of surface environment of active metal sites, and the consequences for catalytic performance, are extremely rare.[7] Most recently, chemical environmental control of metal NPs in MOFs was found to regulate catalytic activity and selectivity.[7] However, to the best of our knowledge, modification of surface hydrophilicity or hydrophobicity with a view to enhancing catalytic activity and/or selectivity of metal NP/MOF composites has not yet been reported.

Herein, a typical MOF (UiO-66)[8] was employed to immobilize Pd NPs, affording a Pd/UiO-66 nanocomposite. A thin layer of polydimethylsiloxane (PDMS), a hydrophobic material, was successfully coated onto Pd/UiO-66 by a facile chemical vapor deposition (CVD) approach, thereby rendering the nanocomposite surface hydrophobic (Scheme 1), based on our recent report.[9] The crystallinity, size of Pd NPs, and Pd site accessibility of Pd/UiO-66 are retained after PDMS coating. Remarkably, the hydrophobic coating facilitates the enrichment of hydrophobic substrates and thereby promotes interaction with Pd sites, while also affording protection and preventing aggregation of Pd NPs. As a result, the PDMS coated Pd/UiO-66 (Pd/UiO-66@PDMS) exhibits significantly improved catalytic efficiency in various reactions and enhanced recyclability compared to the pristine Pd/UiO-66. Remarkably, the PDMS coating endows a diverse range of Pd-based catalysts with the additional ability to differentiate hydrophilic and hydrophobic substrates.

Microporous UiO-66 ($Zr_6O_4(OH)_4(BDC)_6$, BDC = 1,4-benzenedicarboxylate) is one of the most studied MOFs. It possesses an intersecting 3D structure, high thermal and



Scheme 1. Preparative route for Pd/UiO-66@PDMS.

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chemical stability, and high porosity and surface area, which are desirable attributes amenable to immobilization of metal NPs.[8] The incipient wetness method was adopted to stabilize Pd NPs with UiO-66. Typically, Pd^{2+} was absorbed into evacuated UiO-66, followed by Pd^{2+} reduction in an H_2 atmosphere at 200 °C to yield Pd/UiO-66 composite with a 0.71 wt % Pd loading. To coat the PDMS thin layer onto the Pd/UiO-66 composite, a facile CVD process was used at 200 °C with varying lengths of coating time (T), affording Pd/UiO-66@PDMS-T (Scheme 1).

A powder X-ray diffraction (PXRD) pattern of Pd/UiO-66 displays sharp characteristic peaks indexed to UiO-66, demonstrating retention of UiO-66 crystallinity and structure upon Pd NP loading (Supporting Information, Figure S1). The absence of a diffraction peak for Pd species infers the low Pd content and/or the formation of small Pd NPs. The PDMS coating does not cause a change in the PXRD pattern, further supporting a preserved UiO-66 crystalline structure (Supporting Information, Figure S1). The N_2 physisorption isotherms of Pd/UiO-66 and Pd/UiO-66@PDMS are similar in shape and the BET surface areas of the materials present a slight decrease with respect to the parent UiO-66 (Supporting Information, Figure S2). The high surface area of Pd/UiO-66@PDMS suggests that the thin PDMS coating is permeable and does not affect the transportation of molecules.

The contact angle of a water droplet on Pd/UiO-66 is approximately 25°, which quickly increases to 115° and 140° upon PDMS coating by CVD (10 and 20 min, respectively; Figures 1 a–c), clearly suggesting that the PDMS coating transforms the surface character of the nanocomposite from hydrophilic to hydrophobic. Although a longer coating time (> 20 min) results in a plateau contact angle of about 140° (Supporting Information, Figure S3), Pd/UiO-66@PDMS obtained with increasing lengths of coating time displays gradually enhanced hydrophobicity that is discernible in a water–ethyl acetate biphasic mixture: the nanocomposite transfers gradually from the aqueous to the organic phase with longer PDMS coating time (Figure 1 d).

It was envisioned that surface hydrophobization of Pd/UiO-66 by PDMS coating would affect catalytic performance significantly. Styrene hydrogenation, a classical reaction performed over Pd NPs, was initially employed to evaluate the effect of PDMS coating on the catalytic performance of Pd/UiO-66. Under the given reaction conditions (Supporting Information), it took 255 min to realize complete hydrogenation of styrene over Pd/UiO-66. In comparison, the catalyst exhibited greatly improved efficiency after PDMS coating. Activity increased in tandem with catalyst coating time, up to 60 min, at which point the Pd/UiO-66@PDMS-60 composite achieved 100 % conversion in 65 min (reducing reaction time by 75 % compared to pristine Pd/UiO-66). A coating time longer than 60 min leads to decreased catalytic efficiency (Figure 2 a). This fact suggests that, to achieve efficient conversion, coating time should be optimized to generate an ideal PDMS layer thickness that matches the wettability of a particular substrate.

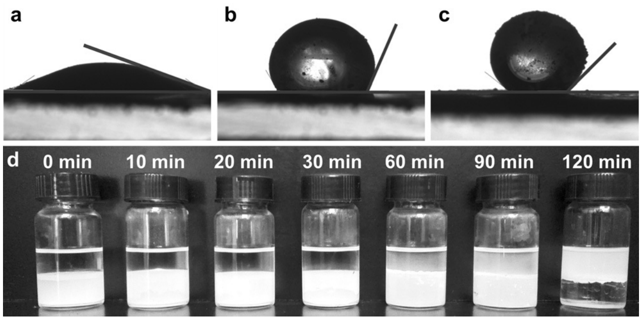

Figure 1. Static water contact angle of a) Pd/UiO-66, b) Pd/UiO-66@PDMS-10, and c) Pd/UiO-66@PDMS-20. d) Photograph of Pd/UiO-66@PDMS-T samples obtained after different durations of PDMS coating time dispersed in a water–ethyl acetate (1:1 v/v) biphasic solution.

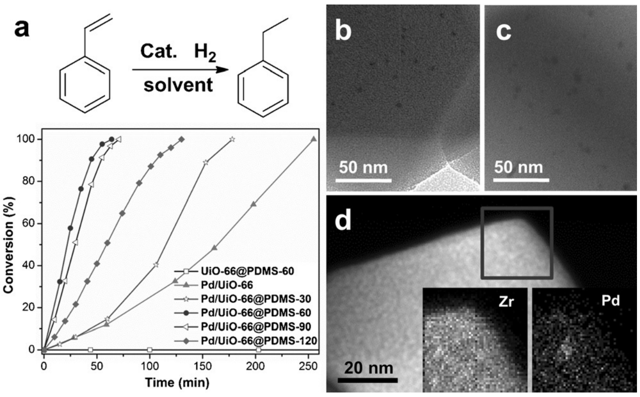

Figure 2. a) Catalytic hydrogenation of styrene over UiO-66@PDMS, Pd/UiO-66, and Pd/UiO-66@PDMS (1:150 Pd:styrene molar ratio). TEM images of b) Pd/UiO-66 and c) Pd/UiO-66@PDMS-60. d) HAADF-STEM image of Pd/UiO-66 (inset: Zr and Pd elemental mapping for the selected rectangular area).

To determine the underlying reasons for such distinct differences in activity before and after PDMS coating, transmission electron microscopy (TEM) was conducted on the materials. Only a few Pd NPs (≤ 5 nm in size) were observed in Pd/UiO-66 (Figure 2 b), which seems unreasonable and might be caused by the similar contrast of Pd NPs and Zr-oxo clusters in UiO-66 upon exposure to an electron beam.[6h] To determine the true nature of the system, elemental mapping was performed and clearly indicates that a mass of tiny Pd NPs, not distinguishable in the aforementioned TEM image, are indeed evenly dispersed within UiO-66 (Figure 2 d; Supporting Information, Figure S4). It is worth noting that, although a small fraction of Pd NPs are larger than the pore sizes of UiO-66, the pore surface structure of the MOF offers spatial restriction to Pd NPs to some extent, in accordance with recent reports describing metal NPs/MOFs.[6] The PDMS coating does not affect the size and distribution of Pd NPs (Figure 2 c; Supporting Information, Figure S5), confirming that Pd NPs remain stable during PDMS encapsulation upon thermal treatment. The elemental mapping images for Pd/UiO-66@PDMS-60 show a uniform Si distribution with a slightly more intense signal at the edges (Supporting Information, Figure S5), which exactly matches our expectations.

X-ray photoelectron spectroscopy (XPS) revealed a clear signal for Si 2p after PDMS coating (Supporting Information, Figure S6), further demonstrating the successful surface modification of Pd/UiO-66. We speculate that the volatile short PDMS chains first produce a conformal layer on the Pd/UiO-66 surface and subsequently crosslink during heat treatment to generate PDMS coatings on the catalyst.[10] The PDMS coating is assumed to contain defects that enable the transportation of catalytic substrates and products. Ar^+ sputtering shows a peak shift in Si 2p, implying that interactions occur between PDMS and the pristine catalyst. The persistent XPS signals for Zr and Pd suggest no change of their electronic states after PDMS coating (Supporting Information, Figure S6).

The size and electronic state of Pd NPs remained after PDMS coating, as indicated above, suggesting that they will not affect catalytic activity. Given the good permeability of the PDMS layer, the H_2 absorption ability of the MOF is similar in both Pd/UiO-66 and Pd/UiO-66@PDMS (Supporting Information, Figure S7).[11] Therefore, the enhanced styrene hydrogenation mediated by Pd/UiO-66@PDMS should primarily be attributed to the hydrophobic PDMS modification on the surface of Pd sites. A hydrophobic surface enables more efficient accumulation of hydrophobic substrate (styrene) and boosts the interaction of that substrate with Pd sites, thereby accelerating catalytic conversion. To some extent, longer coating time leads to a catalyst with a more hydrophobic surface (Figure 1; Supporting Information, Figure S3) and higher activity. Despite this, excessive coating time (> 60 min) produces a thick PDMS layer (Supporting Information, Figure S8), which might block some Pd sites and/or impede the transportation of substrate and product, thus lowering the activity.

The recycling stability of a catalyst is important in practical applications. Pristine Pd/UiO-66 displayed deceasing activity over three repeated runs of styrene hydrogenation because of the aggregation of Pd NPs (Figures 3 a,b). As some Pd NPs with sizes larger than the MOF pores remain on the MOF surface, the migration and growth of Pd NPs is unavoidable during the reaction. In sharp contrast, the Pd/UiO-66@PDMS composite possesses stable activity over three cycles (Figure 3 a; Supporting Information, Figure S9). We believe that the PDMS layer plays a critical role in the stabilization of Pd NPs by encapsulation, which is further supported by good retention of Pd NP size (see TEM images taken after cycling, Figure 3 c). Moreover, the XPS signal for Si 2p in the catalyst does not decay after recycling (Supporting Information, Figure S6c), suggesting that the coating layer does not peel off during the reaction. PXRD and N_2 sorption experiments further support retention of porosity and stability of Pd/UiO-66@PDMS after catalysis (Supporting Information, Figure S10).

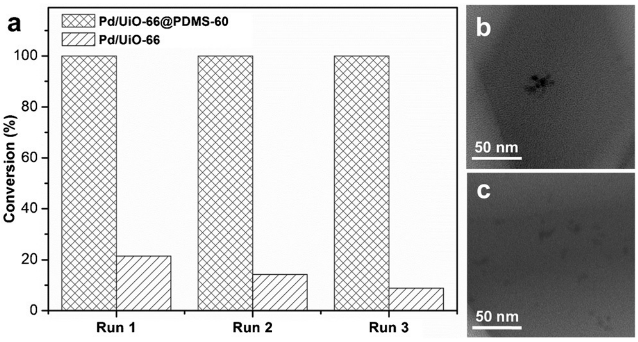

Figure 3. a) Catalytic activity over three consecutive styrene hydrogenation runs using Pd/UiO-66 in the absence or presence of PDMS coating (65 min for each catalytic run). TEM images for b) Pd/UiO-66 and c) Pd/UiO-66@PDMS after recycling experiments.

To determine whether the Pd/UiO-66@PDMS catalyst is extendable to other reactions with hydrophobic substrates, cinnamaldehyde and nitrobenzene (NB) were selected as reactants for hydrogenation (Supporting Information, Figure S11). As expected, Pd/UiO-66@PDMS exhibited superior activity compared to that of Pd/UiO-66 in both reactions. For the selective hydrogenation of cinnamaldehyde, pristine Pd/UiO-66 took as long as 7200 min to reach 100 % conversion (1:50 Pd:substrate molar ratio), while the catalyst coated with PDMS for 10–60 min offered enhanced activity to varying degrees. Pd/UiO-66@PDMS-30 exhibited the best activity and promoted completion of the reaction in 2250 min, a third of the reaction time compared to the PDMS-free catalyst. The optimized PDMS coating time for the Pd/UiO-66 catalyst was found to be 20 min in the case of nitrobenzene hydrogenation. The resulting catalyst, Pd/UiO-66@PDMS-20, promoted full conversion in 60 min (1:150 Pd:NB molar ratio), when compared to pristine Pd/UiO-66, which only yielded about 5 % under identical conditions and required 460 min to reach complete conversion (eight-fold of the reaction time required by the PDMS-coated catalyst).

Encouraged by the improved activity of Pd/UiO-66@PDMS, PDMS coating was attempted to boost the performance of other Pd-based catalysts. Representative examples include, commercial Pd/C and classical Pd/SiO_2, which were coated with thin PDMS layers using a similar approach (Supporting Information, Figure S12). The commercial Pd/C catalyst required 120 min to fully convert styrene into ethylbenzene, while only 60 min was needed for Pd/C@PDMS-10. The difference in activity was even larger for Pd/SiO_2 with or without PDMS coating: Pd/SiO_2 required 150 min to achieve 100 % conversion, whereas catalysis mediated by Pd/SiO_2@PDMS-60 was complete after 70 min. Similar to Pd/UiO-66, the additional stabilization of Pd NPs acquired upon PDMS encapsulation endowed Pd/SiO_2@PDMS with remarkably improved recyclability when compared to pristine Pd/SiO_2 (Supporting Information, Figure S13).

The above results unambiguously demonstrate that the hydrophobic PDMS layer promotes the accumulation and penetration of hydrophobic substrates and thus greatly improves catalytic activity. However, the PDMS coating may hamper the transportation of hydrophilic molecules. To investigate this possibility, hydrophilic 2-butene-1,4-diol was evaluated as a representative substrate in hydrogenation. All substrate was converted in 240 min with Pd/UiO-66 (1:500 Pd:substrate molar ratio). In contrast, PDMS-coated Pd/UiO-66 reached full conversion after 480 min, twice the reaction time needed by the pristine catalyst (Supporting Information, Figure S14). The results suggest that the hydrophobic PDMS coating can boost catalytic performance in reactions where hydrophobic substrates are involved, while it is detrimental to catalysis involving hydrophilic reactants. The mechanism underlying this diametric response lies in the wettability interaction between the catalyst surface and substrates.

Besides the improvements in catalytic hydrogenation activity and recyclability attained with hydrophobic substrates, we were delighted to learn that PDMS coating on Pd catalysts offered wettability-selective catalytic behavior. The hydrogenation of hydrophobic nitrobenzene (NB) and hydrophilic 4-nitrophenol (4-NP) were chosen as model reactions. Under hydrogenation conditions, Pd/UiO-66 was able to reduce both NB and 4-NP (Pd:4-NP (1:10), Pd:NB (1:20) molar ratios) into their respective products, and the complete conversion of 4-NP was faster (6.5 min) than that for NB (180 min; Figure 4a; Supporting Information, Figure S15). Upon PDMS coating, the same reaction with the hydrophobic NB was completed in 60 min (Figure 4b; Supporting Information, Figure S16a), inferring that hydrophobic NB can pass through the PDMS layer. In stark contrast, the reduction of hydrophilic 4-NP over Pd@UiO-66@PDMS did not proceed, as evidenced by a negligible change in the characteristic UV/Vis peak of 4-NP during 24 h of reaction (Figure 4b; Supporting Information, Figure S16b). Given the high activity of Pd NPs toward the reduction of 4-NP reported elsewhere,[12] this result indicates that the hydrophobic PDMS shell of the catalyst impedes the transportation of hydrophilic 4-NP and thus the Pd active sites become unavailable to 4-NP. Therefore, the PDMS coated Pd-based catalyst promotes high catalytic selectivity for hydrophobic molecules but excludes hydrophilic molecules. Further to this, the PDMS coated Pd@UiO-66 catalyst, where Pd NPs are incorporated inside UiO-66,[13] not only offers wettability-selective catalytic behavior (Supporting Information, Figures S17–19), but also possesses intrinsic size selectivity for sieving catalytic substrates of different sizes (Supporting Information, Figure S20).[11a,13a] Therefore, Pd@UiO-66@PDMS possesses dual wettability- and size-selectivity toward different reaction substrates. This pronounced size selectivity behavior has been further demonstrated in the hydrogenation of diverse olefins over Pd@ZIF-8 and Pd@UiO-66 with different MOF pore sizes (Supporting Information, Figure S21).

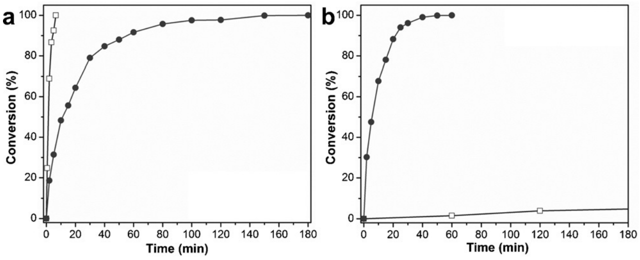

Figure 4. A comparison of catalytic reduction of nitrobenzene (——●——) and 4-nitrophenol (——□——) over a) Pd/UiO-66 and b) Pd/UiO-66@PDMS-60.

In summary, modification of surface hydrophobicity of Pd NP catalysts was developed using a facile PDMS coating approach. The MOF-stabilized Pd NPs are encapsulated by a thin hydrophobic PDMS layer, which makes the surface of the catalyst hydrophobic and thus creates enhanced affinity for hydrophobic substrates. As a result, Pd/UiO-66@PDMS shows significantly improved activity compared to pristine Pd/UiO-66 in various reactions. PDMS coating leads to improved catalytic recyclability as well as novel wettability selectivity for hydrophobic and hydrophilic substrates. Further experiments indicate that the PDMS-coating approach is not confined to Pd/MOF, being an ideal candidate to demonstrate the applicability of surface hydrophobization (Supporting Information, Section 4), and can be extended to various Pd nanoparticulate catalysts, such as commercial Pd/C and Pd/SiO_2. We envision that this facile surface hydrophobization PDMS coating approach could be extended to other types of catalysts and that this work would open a new avenue to enhanced activity and stability, as well as additional selectivity in catalysis.

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