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Controlling Catalytic Properties of Pd Nanoclusters through Their Chemical Environment at the Atomic Level Using Isoreticular Metal–Organic Frameworks

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ABSTRACT: Control of heterogeneous catalytic sites through their surrounding chemical environment at an atomic level is crucial to catalyst design. We synthesize Pd nanoclusters (NCs) in an atomically tunable chemical environment using isoreticular metal–organic framework (MOF) supports (Pd@UiO-66-X, X = H, NH2, OMe). In an aerobic reaction between benzaldehyde and ethylene glycol, these catalysts show product distributions that are completely altered from the acetal to the ester when we change the functional groups on the MOF linkers from –NH2 to –H/–OMe. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies, along with density functional theory (DFT) calculations, show that the coordination of the –NH2 groups to the Pd NCs could weaken their oxidation capability to a greater extent in comparison to that of the –OMe group. Moreover, the limited number of –NH2 groups per cavity in the MOF change the electronic properties of the Pd NCs while still leaving open sites for catalysis.

KEYWORDS: isoreticular metal–organic framework, under-coordinated metal nanoclusters, DRIFTS studies, DFT, atomic-level selectivity control, oxidation, acetalization, structure–activity relationship

INTRODUCTION

Developing an atomic- and electronic-level understanding of catalysis is necessary for the design of effective catalysts with atomic precision to exercise molecular control during catalytic reactions. These atomic- and molecular-level controls have been partially realized in enzymatic and homogeneous catalysis. For example, the inherent activity of an enzyme can be modulated by protein engineering and immobilization.1,2 In homogeneous catalysts, steric and electronic effects of the ligands play a decisive role in their activity and stereoselectivity, thus establishing structure–activity relationships between homogeneous catalysts and their catalytic properties.3–5 However, in heterogeneous catalysts, it is relatively hard to achieve an atomic-level understanding about the effect of the chemical environment surrounding the catalytic sites on their catalytic performance, largely due to the lack of a catalyst support with atomic-level tunability. Unlike traditional catalyst supports, metal–organic frameworks (MOFs), featuring precisely controlled and tunable crystal structures and compositions, are an ideal platform to study the effect of the chemical environment surrounding the catalytic sites on their catalytic properties.6

MOFs are a burgeoning class of hybrid porous materials and have spurred tremendous research interest in the realm of heterogeneous catalysis.9–12 The use of MOFs as novel hosts for metal nanoparticles (NPs) has been extensively investigated.13–18 In comparison to other porous materials such as zeolites and mesoporous silica, the properties of MOFs are rationally “designable” to study the effect of the chemical environment on the encapsulated metal NPs or nanoclusters (NCs) because the metal ions and the organic linkers of MOFs can be fine-tuned either by utilizing different building units or by the postsynthetic modification of presynthesized MOFs.19–21 The introduction of different functional groups in isoreticular MOFs can dramatically affect the gas sorption capacity and uptake selectivity,22,23 luminescence,24 water stability,25 and mechanical properties of the MOFs.26 However, studies on the effects of introducing different functional groups in isoreticular MOFs on catalysis have been rarely reported.27–29 In pioneering work carried out by the groups of De Vos and...
Jhung, it was found that Lewis acid catalysis can be affected by changing the organic linkers in zirconium-based UiO-66 MOFs. Nonetheless, varying product selectivity controlled through the well-defined chemical environment of isoreticular MOFs has scarcely been reported in heterogeneous catalysis to date. In the present study, we provide spectroscopic and theoretical investigation for the first time, which could explain the different catalytic properties of Pd NCs when they are confined in different chemical environments of isoreticular MOFs.

Here we have developed isoreticular MOFs containing palladium NCs (denoted as Pd@UiO-66-X, X = H, NH2, OMe) as catalysts for the aerobic reaction between benzaldehyde and ethylene glycol. By varying the functional group on the organic linkers of the UiO-66-X MOFs from −NH2 to −H/−OMe, the product selectivity was completely altered from an acetal to an ester. The distinct product distribution is attributed to the different oxidation capability derived from Pd NCs encapsulated in the isoreticular MOFs and NH2−Pd interactions inhibiting the formation of esters. It is noteworthy that the NH2−Pd interactions hindered but did not completely impair the oxidation capacity of Pd NCs. Modifying the organic linkers in UiO-66 results in geometrically identical cages with functionally diverse chemical environments. Pd NCs, encapsulated in these MOFs, are surrounded by different chemical environments and thus exhibit different activities and selectivities in catalytic reactions.

### EXPERIMENTAL SECTION

#### Materials and Synthesis

Synthesis of UiO-66-X (X = H, NH2, OMe). UiO-66-X (X = H, NH2, OMe) was synthesized and purified according to a protocol reported by Lillerud and De Vos et al. Typically, UiO-66-X was synthesized under solvothermal conditions: zirconium(IV) chloride (0.40 g, 1.71 mmol, 98%, Acros Organics) and the corresponding organic linker (H, NH2, OMe-H2BDC, 1.71 mmol; OMe-H2BDC was synthesized according to previously reported work) were dissolved in 100 mL of N,N-diethylformamide (DMF, ACS grade, Macron) by sonication for 5 min in a wide-mouth Teflon PFA jar. For the synthesis of UiO-66-NH2, a small amount of water (0.13 mL, 6.84 mmol) was added to the solution and 1.8 mL of acetic acid was added as a modulator in the synthesis of UiO-66-OMe. The tightly capped jar was placed in a preheated oven at 120 °C for 24 h. After the jar was cooled to ambient temperature, the solid MOFs were collected via centrifugation and were thoroughly washed with DMF (three times) and methanol (three times) every 12 h. Finally, the MOFs were activated at 150 °C under vacuum (30 mTorr) for 12 h prior to experimental use.

Preparation of Pd NCs@UiO-66-X (X = H, NH2, OMe). Around 100 mg of activated UiO-66-X was dispersed in 5 mL of methylene chloride and was sonicated for 1 h to achieve a homogeneous dispersion. Palladium acetate solution (4.32 mg of Pd(OAc)2, Oakwood Chemical, in 5 mL of methylene chloride) was added dropwise to the above solution with vigorous stirring (800 rpm). After 24 h of stirring at ambient temperature, the as-prepared Pd-infiltrated MOF was washed three times every 12 h by centrifugation to remove the remaining palladium salts completely. The solid was air-dried and reduced under a 50 mL/min flow of 10% H2/Ar at 200 °C for 2 h.

#### Instrumentation.

Surface area analysis of the catalysts was performed by N2 adsorption/desorption isotherms using a Micromeritics 3Flex surface characterization analyzer at 77 K. Powder X-ray diffraction patterns of the samples were obtained by a STOE Stadi P powder diffractometer using Cu Kα radiation (40 kV, 40 mA, λ = 0.1541 nm). The size and morphology of Pd@UiO-66-X were investigated using transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images recorded on a Tecnai G2 F20 electron microscope equipped with an energy-dispersive X-ray (EDX) detector (Oxford INCAEDS). ICP-MS (X Series II, Thermo Scientific) was performed to determine the actual loading of palladium in UiO-66-X. The ICP-MS sample was prepared by dissolving the Pd@UiO-66-X samples in boiling aqua regia until the solid was completely dissolved. The X-ray absorption spectra (XAS) were measured in transmission mode (Pd K-edge 24.350 keV) at the 20-BM-B and 9-BM-B beamlines of the Advanced Photon Source at Argonne National Laboratory. XAS of reference samples were collected using pure finely ground powders homogeneously dispersed on polyimide Kapton tape. The MOF samples were pressed into a pellet fit to a hole embedded in a Teflon substrate. A palladium foil spectrum was acquired simultaneously with each measurement for energy calibration. Multiple scans (8–10 scans) were collected for each sample and merged into one data set for XAS analysis. For XAS analysis, the software at the beamline in Argonne National Laboratory was used to perform dead-time correction and energy calibration. The Athena program, which is an interface to IFEFFIT and FEFFIT, was used for glitch removal, pre-edge subtraction, postedge normalization, and conversion to k space. The EXAFS data were fitted in R space by using the Artemis program from the same package, with theoretical models constructed from FEFF6. All of the EXAFS data fittings were performed with a k3 weighting in R space. The k ranges (Å−1), R ranges, independent points in the EXAFS spectrum, the number of variables determined in the models, and the fitting quality are given in Table S2 in the Supporting Information. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed using an Agilent Cary 670 FTIR equipped with a linearized MCT detector, a Harrick diffuse reflectance accessory, and a Praying Mantis high-temperature reaction chamber. MOF samples were packed in the sample cup, followed by an activation process under high vacuum (10−6 mTorr) at 150 °C for 1 h to remove the absorbed water. After the sample was cooled to ambient temperature, the spectra were recorded at 2 cm−1 resolution within the range of 4000−700 cm−1. Kubelka−Munk correction was applied to generate the spectra for qualitative analysis.

#### Computational Methods.

Density functional theory (DFT) methods were used to perform geometry optimization and computation of the electronic properties. More specifically, the plane-wave basis sets and projected augmented wave (PAW) pseudopotentials implemented in the Vienna ab initio simulation package (VASP 5.3) were adopted. The exchange-correlation interaction was treated within the generalized gradient approximation (GGA) in the Perdew−Burke−Ernzerhof (PBE) form. Spin-restricted computation with the energy cutoff at 400 eV was selected. Aniline, anisole, and the Pd38 cluster with high octahedral symmetry were chosen to simulate Pd interactions hindered but did not completely impair the oxidation capacity of Pd NCs. Modifying the organic linkers in UiO-66 results in geometrically identical cages with functionally diverse chemical environments. Pd NCs, encapsulated in these MOFs, are surrounded by different chemical environments and thus exhibit different activities and selectivities in catalytic reactions.
on each atom was less than 0.02 eV/Å. The chemical potential is calculated as
\[ \mu = \frac{-I + A}{2} = \frac{E(N + 1) - E(N - 1)}{2} \]
where \( I, A, E(N + 1), \) and \( E(N - 1) \) represent ionization energy, electron affinity, and the energies of the \( N + 1 \) and \( N - 1 \) electron systems, respectively. The \( N + 1 \) and the \( N - 1 \) electron systems correspond to the same system with one positive and negative net charge, respectively.

**Catalysis.** Typically, 10.5 mg of benzaldehyde (0.1 mmol, >99%, Aldrich), 1.5 mL of ethylene glycol (Fisher Scientific), Pd@UiO-66-X (Pd/substrate 1/100), and 7 mg of mesitylene (internal GC standard, 99%, Acros Organics) were placed in a 20 mL glass vial. The air in the vial was removed by using a modified freeze-pump method. The vial with an oxygen balloon on top was loaded in an oil bath which was preheated to 90 °C, and then the reaction was carried out with magnetic stirring at 600 rpm. After the reaction was finished, the products were analyzed using a gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) with a flame ionization detector and Shimadzu 5050A GC-MS instrument equipped with an HP-5 ms capillary column (30 m × 0.32 mm × 0.25 μm).

**Control Experiments with Benzaldehyde and Ethylene Glycol without O2.** A freeze–pump–thaw method was applied to remove O2 completely in the system. Typically, 10.5 mg of benzaldehyde (0.1 mmol, >99%, Aldrich), 1.5 mL of ethylene glycol (Fisher Scientific), and Pd@UiO-66-X (Pd/substrate 1/100) were placed in a 20 mL glass vial. The mixture was frozen with liquid nitrogen and connected to a Schlenk line. The vial was then subjected to vacuum for 5 min to remove all traces of oxygen, following which the flask was sealed. Then the solvent was thawed until it just melted using a water bath, and this was purged with argon gas for 5 min before the solvent was frozen again. This freeze–pump–thaw process was repeated three times, and then the vial with an argon balloon on top was loaded in an oil bath which was preheated to 90 °C and the reaction was carried out.

**Probe Alkene Hydrogenation.** Styrene (0.1 mmol, 98%, Aldrich) and palladium catalyst (Pd/substrate 1/100) were added to 1.5 mL of ethanol, and the reaction mixture was stirred at 50 °C with a hydrogen balloon for 15 h. Upon the completion of styrene hydrogenation, the solid catalyst was removed from the solution by filtration and the liquid phase was analyzed using a gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) with a flame ionization detector. For tetraphenylethylene (0.1 mmol, >99%, Aldrich), the Pd@UiO-66-X sample was packed in a 20 mL glass vial. The air in the vial was removed by using a freeze–pump–thaw method. The vial with an oxygen balloon on top was loaded in an oil bath which was preheated to 90 °C, and then the reaction was carried out with magnetic stirring at 600 rpm. After the reaction was finished, the products were analyzed using a gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) with a flame ionization detector and Shimadzu 5050A GC-MS instrument equipped with an HP-5 ms capillary column (30 m × 0.32 mm × 0.25 μm).

**Co Adsorption Studies of the Pd@UiO-66-X Catalyst.** The Pd@UiO-66-X (X = H, NH2, OMe) sample was synthesized using a protocol that has been previously reported by our group.11 The powder X-ray diffraction (PXRD) analyses showed that UiO-66-X was successfully prepared and there were no obvious changes in the PXRD patterns of Pd@UiO-66-X after the impregnation and reduction of Pd(II) (Figure S1 in the Supporting Information), consistent with reported literature.44 The N2 sorption isotherms of all samples show a type I pattern (Figure S2 in the Supporting Information). The appreciable decrease in the BET surface area and the pore volume of Pd@UiO-66-X compared to the pristine MOFs (Table S1 in the Supporting Information) are likely due to the occupation of Pd NCs in MOF cavities and/or block of the MOF pores by these NCs, as in the case of metal NPs loaded into ZIF-8, MIL-101, and UiO-66-NH2.29,41,42 The UiO-66-X MOFs reveal two major pores at 7~10 and ~12 Å, which agree well with reported works.43,44 In comparison to pristine MOFs, Pd@UiO-66-X show decreased pore volumes due to the occupation of Pd NCs in the cavities of the MOFs (Figure S3 in the Supporting Information). Pd NCs with an average size of less than 1.2 nm (the diameter of the largest octahedral cages in UiO-66-X MOFs) are uniformly dispersed in UiO-66-X, as revealed by the TEM images (Figure S4 in the Supporting Information). The fact that the size of the Pd NCs is smaller than the diameter of the cavities in the MOFs is a strong indication that the formed Pd NCs are well dispersed inside the cavities of the UiO-66-X MOFs. HAADF-TEM images of Pd@UiO-66-NH2 confirm that there is no particle larger than 1.2 nm (Figure S5 in the Supporting Information). From the EDX mapping of selected area on the Pd@UiO-66-NH2 (Figure S6 in the Supporting Information), palladium NCs were uniformly dispersed inside the MOF and no sign of aggregation was observed.

**Probe molecules of different sizes have been extensively used to confirm the location of catalytically active sites inside MOFs16,45–47 and zeolites.48 To further confirm that the Pd NCs are confined in the cavities of MOFs, we utilized Pd@UiO-66-X and commercially available Pd/C to hydrogenate two probe molecules of different sizes: styrene (4.2 Å in atomic diameter; 6.0 Å in kinetic diameter)19 and tetraphenylethylene (6.7 Å in atomic diameter).50 Tetraphenylethylene is too bulky to diffuse through the aperture of UiO-66-X (6.0 Å) and thus should not be hydrogenated by the Pd NCs confined inside the MOFs, whereas the relatively smaller styrene molecule can readily access the encapsulated Pd NCs and undergo hydrogenation conveniently (Scheme 1). As expected (Figure 1), all Pd@UiO-66-X and Pd/C catalysts displayed high activity (100% conversion) in the hydrogenation of styrene. However, Pd@UiO-66-X showed no detectable activity in the
hydrogenation of tetraphenylethylene, while Pd/C and Pd NPs deposited on the external surface of UiO-66-NH2 (Pd/UiO-66-NH2) still had relatively good activity (38% and 28% conversion, respectively; Figure S7 in the Supporting Information), implying that the Pd NCs are indeed encapsulated inside the cavities of UiO-66-X MOFs.

We used extended X-ray absorption fine structure (EXAFS) spectroscopy to explore the coordination environment of Pd in UiO-66-X before and after the reduction step. As shown in Figure S8a,c,e in the Supporting Information, EXAFS spectra of the three catalysts before reduction have a dominant Pd−O scattering peak (2.0 Å), which is in good agreement with the structure of the Pd precursor, palladium acetate. After reduction with a 10% H2/Ar flow at 200 °C, the scattering of Pd−Pd appears in Fourier transform as shown in Figure S8b,d,f. EXAFS fitting showed that Pd−Pd scattering has a interatomic distance of 2.78 ± 0.01 Å, indicating the formation of Pd NCs.

To investigate the effects of the chemical environment surrounding Pd NCs on their catalytic properties, we carried out an aerobic reaction between benzaldehyde and ethylene glycol over Pd@UiO-66-X (X = H, NH2, OMe). As shown in Figure S9 in the Supporting Information, the plausible mechanism of this reaction involves two steps:51,52 (i) condensation of benzaldehyde and ethylene glycol to yield hemiacetal or oxidation to yield ester. After screening the reaction temperature, we chose 90 °C since the lower temperature (e.g., 65 °C) gave lower product yield, while higher temperature (e.g., >100 °C) facilitated MOF degradation and Pd NC aggregation. As shown in Figure 2b and Table S3 in the Supporting Information (entries 1−3), Pd@UiO-66-X (X = H, NH2, OMe) catalysts gave high conversions (99%, 91%, and 98%, respectively) with distinctly different product distributions: i.e., Pd@UiO-66-NH2 gave the corresponding acetal, benzaldehyde ethylene acetal (selectivity 94%), as the major product, while Pd@UiO-66-H and -OMe showed high selectivity (90% and 97%, respectively) to the corresponding ester, 2-hydroxyethyl benzoate. These product distributions, particularly for Pd@UiO-66-NH2, were still retained even if the reaction time was extended from 10 to 60 h, indicating that Pd NCs in UiO-66-NH2 do not have the ability to oxidize the hemiacetal to the ester.

However, it is worth mentioning that Pd@UiO-66-NH2 is active for the oxidation of benzyl alcohol to benzaldehyde, which will be discussed later. In the kinetic studies (Figure S10 in the Supporting Information), all catalysts achieved high conversion of benzaldehyde within 1 h and produced acetal as the predominant product. For Pd@UiO-66 and Pd@UiO-66-OMe, the acetal was gradually converted to the ester due to the reversible nature of the hemiacetal−acetal conversion, while for Pd@UiO-66-NH2, acetal quantities were always significantly greater than that of the ester. We used UiO-66-X alone to catalyze the aerobic reaction but only obtained acetal, confirming that the Pd NCs are the active sites in the formation of the ester (Table S3 in the Supporting Information, entries 4−6).

We also carried out anaerobic reactions with benzaldehyde and ethylene glycol using Pd@UiO-66-X and Pd/C in the presence of argon, and we did not see any formation of ester but acetal (Table S3, entries 7−9 and entry 13), which implies that O2
was indispensable in the formation of ester in the second step of the reaction, especially for Pd@UiO-66 and Pd@UiO-66-OMe.

Through the proposed reaction mechanism (Figure S9 in the Supporting Information), we initially postulated that the final product distribution depends on the competition between hemiacetal oxidation and self-condensation. When the oxidation of hemiacetal precedes acetalization, the ester will be the predominant product and vice versa. From the kinetic studies (Figure S11 in the Supporting Information), we determined that the rate constants of acetalization over Pd@UiO-66, Pd@UiO-NH$_2$, and Pd@UiO-OMe are 0.259, 0.199, and 0.123 min$^{-1}$, respectively. The fact that UiO-66 is more active than UiO-66-NH$_2$ in our acetalization reaction is consistent with a recent study by Jhung et al.$^{31}$ but cannot explain why the ester is the major product for Pd@UiO-66.

Given that the acetalization activity of the MOFs is not the key factor that determines whether acetal or ester is the major product, we proceeded to investigate the oxidation capacity of the encapsulated Pd NCs. Aniline (1 equiv of Pd), which mimics the linker units in UiO-66-NH$_2$, was added deliberately to the reactions catalyzed by Pd@UiO-66 and Pd@UiO-66-OMe (Table S3 in the Supporting Information, entries 10 and 11). We found that ester formation was totally precluded, indicating that the NH$_2$−Pd interaction inhibits the oxidation capability of Pd NCs encapsulated in UiO-66 and UiO-66-OMe. Pd/C, which does not contain a NH$_2$−Pd interaction, still gave the ester as the major product (Table S3, entry 12). However, Pd/C gave no ester at all in the presence of aniline (1 equiv of Pd) (Table S3, entry 14). Therefore, we speculated that the product distribution is determined by the different oxidation capability derived from Pd NCs encapsulated in the three isoreticular UiO-66-X MOFs. Since the Pd NCs are embedded in the cavities of the MOFs, the chemical environment endowed by the MOFs is prone to change the adsorption of reactants and the surface electronic property of the Pd NCs, thus controlling their oxidation capability. To verify our speculation, we employed aerobic benzyl alcohol oxidation in isopropyl alcohol as a test reaction to evaluate the oxidation capacity of Pd NCs residing in UiO-66-X (Figure S12 in the Supporting Information). We found that these Pd NCs in different substituted MOFs displayed distinct oxidation capacities, and the trend in the oxidation capacity is consistent with the order shown in Figure 2 (Pd@UiO-66 > Pd@UiO-66-OMe > Pd@UiO-66-NH$_2$). We did not detect any benzoic acid in this reaction, which agrees with a previous report.$^{53}$ Considering that the blank test and pristine MOFs show negligible activity, we actually tuned the oxidation capacity of Pd NCs using isoreticular MOFs.

We envision that confining metal NCs in the cavities of MOFs represents a new way to control the coordination of functional groups to the metal surface because of the defined crystal structure of MOFs. In this work, the octahedral cage with 12 linkers in UiO-66-NH$_2$ has a defined number of −NH$_2$ groups (12) that could coordinate to the confined Pd cluster. This new strategy is completely different from that for the metal nanoparticles prepared in colloidal solution, where the metal surface is saturated with ligands/functional groups and could be completely poisoned if all active sites are occupied. To validate this hypothesis, we intentionally added various amounts of aniline (0.2, 0.4, 0.6, 0.8, and 1 equiv of Pd) to Pd@UiO-66-NH$_2$ in the oxidation of benzyl alcohol under identical conditions (Table S4 in the Supporting Information). As expected, the conversion of benzyl alcohol decreased as the aniline amount increased. Pd@UiO-66-NH$_2$ gives 90% conversion in 10 h (Table S4, entry 1) while Pd-aniline@UiO-66-NH$_2$ was almost inactive (aniline/Pd = 1, 5% conversion in 10 h, Table S4, entry 6). These control experiments highlight the advantages of using the undercoordinated Pd NCs confined in MOFs as catalysts, where we can tune the catalytic properties of these Pd NCs through ligand−surface interaction without completely blocking their surface active sites.

Bearing these findings in mind, we sought to investigate the Pd NC−MOF interaction, which may account for the different product distributions. Since such an interaction could not be elucidated from EXAFS due to the close approximation between Pd−O and Pd−N (Figure S8 in the Supporting Information), we used DRIFTS to probe the Pd NC−MOF interaction. As shown in Figure 3, the peaks at 2843 cm$^{-1}$ and 1560 cm$^{-1}$ (indicated by the dashed lines), corresponding to the respective O−C−O symmetric and asymmetric stretching vibrations, have shifted to higher wavenumbers, while peaks at 3395 cm$^{-1}$ and 3505 cm$^{-1}$, corresponding to N−H symmetric and asymmetric stretches, respectively, have shifted to lower energy.$^{27,54}$ These shifts in Pd@UiO-66-NH$_2$ indicate that there could be an interaction between the Pd NCs with the −NH$_2$ on the benzenedicarboxylate moiety in the MOF.$^{49}$ The coordination of −NH$_2$ on the linker of the MOF with the Pd surface could affect the adsorption of reactants and thus the catalytic properties of these Pd NCs.

To further probe the surface electronic properties of encapsulated Pd NCs, we used DRIFTS to study the adsorbed CO molecules on the Pd@UiO-66-X (Figure 4). CO adsorption spectra of all three samples do not show any vibration peaks above 2143 cm$^{-1}$, which indicates the absence of CO adsorption on any possible cationic species in the sample, such as Pd$^{2+}$. $^{55}$ Peaks in the 2020−2075 cm$^{-1}$ region correspond to C−O vibrations of linearly adsorbed CO, while peaks in the 1850−1950 cm$^{-1}$ correspond to the C−O vibration of 2-fold bridge carbonyls on the Pd$^{2+}$ surface.$^{36−60}$ The DRIFTS spectra shows that the C−O vibration for CO adsorbed on Pd NCs in UiO-66-NH$_2$ exhibits a shift to a lower wavenumber (2059 cm$^{-1}$) in comparison to those in UiO-66-OMe and UiO-66 (2071 and 2073 cm$^{-1}$, respectively).$^{60}$ The decrease in CO vibration wavenumber indicates that the C−O bond is weakened by the π back-donation from the electron-enriched
surface of Pd NCs in UiO-66-NH₂ in comparison to those in UiO-66 and UiO-66-OMe. The −NH₂ group, with a lone pair of electrons, could donate these electrons to the Pd NC surface, which agrees with the lower N−H stretching vibration wavenumbers in Pd@UiO-66-NH₂ in comparison to those in pristine UiO-66-NH₂ (Figure 3, inset). We also found that the IR spectrum for CO adsorbed on Pd@UiO-66-NH₂ contains less fine structures in comparison to those on Pd@UiO-66-OMe and Pd@UiO-66 (Figure 4). This could be due to the strong interaction of −NH₂ with Pd that can block the adsorption of CO at certain surface sites on Pd NCs confined in UiO-66-NH₂.

Our DRIFTS studies suggested that the interactions between −NH₂ and Pd NCs in UiO-66-NH₂ affect the reactant adsorption and donation of electrons to the metal surface, which could lead to their hindered activity in the oxidation of hemiacetal to ester. More importantly, these interactions did not completely impair the oxidation capacity of Pd NCs, as evidenced by the fact that Pd@UiO-66-NH₂ is still active for oxidation of benzyl alcohol to benzaldehyde under the same reaction conditions but using benzyl alcohol as the starting material (Figure S13 in the Supporting Information).

In the oxidation reaction, the catalysts generally act as an electron reservoir, which requires a moderate oxidation capability of the catalysts to charge and discharge the reactants during the reaction cycle. To gain deeper insight into the effect of different functional groups on the oxidation capability of Pd NCs, we computed the evolution of the d-band center and the chemical potential change associated with the number of functional groups (−NH₂ or −OMe) on the highly symmetric Pd₃₈ cluster as a prototype model system. All computations were performed at the level of DFT (see Figure S14 in the Supporting Information for detailed methods and two model systems, denoted Pd₃₈-NH₂ and Pd₃₈-OMe). As shown in Figure 5, for both systems, the d-band center of the Pd₃₈ clusters shifts toward higher energy levels with an increase in the number of functional groups due to the electron donation from the functional groups (Figure S15 in the Supporting Information). Such a shift of the d-band center to higher energy levels leads to increased chemical potential for the functionalized Pd₃₈ clusters and thereby the tendency to lose more electrons. In other words, the increased chemical potential results in the impairment of the oxidation properties of Pd NCs.

However, an important difference observed between the two systems is that, with the same number of functional groups, the −NH₂-functionalyzed MOF results in a greater increase in the chemical potential in comparison to the −OMe-functionalyzed MOF. Additionally, such a difference between the two systems becomes more evident with an increase in the number of functional groups. Hence, strong reduction coupled with weak oxidation is expected for the Pd@UiO-66-NH₂ system, whereas the relatively weak oxidation property can impede drawing electrons from reactants, thus hindering completion of the reaction cycle. In contrast, moderate oxidation capability can be achieved in the Pd@UiO-66-OMe system to facilitate both the charging and discharging processes of the reactants. Hence, the Pd@UiO-66-OMe system exhibits higher catalytic activity toward the formation of esters.

We further extended our strategy to another catalytic transformation, gas-phase furfural hydrogenation catalyzed by Pd@UiO-66-X (X = H, NH₂, OMe), where the desired product of the hydrogenation was furfuryl alcohol. Unsurprisingly, these chemical functionalities in the linker play a critical role in product selectivity and activity in the gas-phase furfural hydrogenation (Figure S16 in the Supporting Information). We controlled the conversion of furfural to be 9.5% at 140 °C for the three catalysts by using different amounts of catalysts. At the same conversion, Pd@UiO-66-NH₂ gave the highest selectivity to furfuryl alcohol (ca. 70%) while Pd@UiO-66 showed the highest selectivity to propane (ca. 55%). We are conducting more computational investigations currently to explore the reasons for such different selectivities to the desired furfuryl alcohol, with regard to steric hindrance and electronic effects.

Finally, the durability of Pd@UiO-66-X (X = H, NH₂, OMe) was evaluated. Pd@UiO-66-X could be recycled at least five times without significant changes in activity and selectivity (Figure S17 in the Supporting Information). Furthermore, the structural integrity of the catalysts was still maintained after the reaction, as evidenced by PXRD (Figure S18 in the Supporting Information). The slight aggregation of Pd NCs after the reaction did not affect the recyclability of the catalysts (Figure S19 in the Supporting Information). In order to confirm that the majority of Pd NCs are still encapsulated inside MOFs, we also performed the encapsulation test by utilizing the used Pd@UiO-66-X as catalysts to hydrogente two probe molecules, styrene and tetraphenylenethylene (Figure S20 in the Supporting Information).
The used Pd@UiO-66-X showed high activity in the hydrogenation of styrene but no detectable activity in the hydrogenation of tetraphenylethylene, suggesting that the majority of the Pd NCs are still encapsulated inside the cavities of UiO-66-X. We speculate that the slight aggregation of Pd NCs in used catalysts may result from the loss of MOF restriction associated with the linker dissociation in the MOF at elevated reaction temperature.41 The N$_2$ sorption analysis showed that the used Pd@UiO-66-X catalysts are still highly porous and the slight decrease of BET surface area and pore volume could be due to the residual reactants or products trapped inside the UiO-66-X (Table S1 and Figure S21 in the Supporting Information), which is consistent with our previous work.41 Pd leaching was assessed after the reaction by ICP-MS analysis of the metal content in the reaction solution after removing the catalysts by centrifugation. The leached Pd in the solution was found to be negligible (<0.1% of total Pd in the added catalysts).

■ CONCLUSIONS

In conclusion, we have developed Pd NCs encapsulated in isoreticular MOFs of different chemical environments (Pd@UiO-66-X, X = H, NH$_2$, OMe), which were used to catalyze the aerobic reaction between benzaldehyde and ethylene glycol. Notably, the linker modification in MOFs can atomically tune the product distribution in this reaction. We found that Pd@UiO-66-NH$_2$ favors the formation of acetal, while Pd@UiO-66 and Pd@UiO-66-OMe have a higher selectivity to ester. DRIFTS studies revealed that –NH$_2$ groups coordinate to the Pd surface and donate electrons to the Pd NCs in Pd@UiO-66-NH$_2$. These NH$_2$–Pd interactions decrease (but do not completely eliminate) the oxidation capability of encapsulated Pd NCs and lead to the high acetal selectivity by Pd@UiO-66-NH$_2$ in the reaction. DFT calculations show that the Pd-NH$_2$ NCs possess higher chemical potential and thus weaker oxidation capability than the Pd-OMe NCs, which agrees with the experimental results. This strategy can be extended to gas-phase furfural hydrogenation, and linker modification in MOFs is decisive to the product distribution as well. The present work demonstrates the control of heterogeneous catalytic sites through their surrounding chemical environment at an atomic level, thus opening up fascinating opportunities for the development of tunable metal-MOF catalysts for selective chemical transformations.

■ ASSOCIATED CONTENT

4 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acskatal.6b00397.

PXRD, EXAFS, nitrogen sorption, TEM images for the catalyst after reaction, kinetics, and recycle tests (PDF)

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Notes

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■ REFERENCES
