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Probing the evolution of palladium species in Pd@MOF catalysts during the Heck coupling reaction: An operando X-ray absorption spectroscopy study

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ABSTRACT: The mechanism of the Heck C–C coupling reaction catalyzed by Pd@MOFs has been investigated using operando X-ray absorption spectroscopy (XAS) and powder X-ray diffraction (PXRD) combined with transmission electron microscopy (TEM) analysis and nuclear magnetic resonance (1H NMR) kinetic studies. A custom-made reaction cell was used allowing operando PXRD and XAS data collection using high-energy synchrotron radiation. By analyzing the XAS data in combination with ex situ studies, the evolution of the palladium species is followed from the as-synthesized to its deactivated form. An adaptive reaction mechanism is proposed. Mononuclear Pd(II) complexes are found to be the dominant active species at the beginning of the reaction, which then gradually transform into Pd nanoclusters with 13–20 Pd atoms on average in later catalytic turnovers. Consumption of available reagent and substrate leads to coordination of Cl ions to their surfaces, which causes the poisoning of the active sites. By understanding the deactivation process, it was possible to tune the reaction conditions and prolong the lifetime of the catalyst.

INTRODUCTION

Sustainable catalysis by transition metals1 is essential for further advances in the large-scale production of specialty chemicals for pharmaceuticals, advanced materials or agrochemicals. In this context, C–C coupling reactions remain indispensable for creating the backbone of organic molecules. To minimize, recycle or replace the heavy metals involved in these processes, for economic and environmental reasons, a thorough understanding of reaction mechanisms is required. The Heck coupling is one such process of utmost importance, forging new C–C bonds between aryl halides and olefins, in the presence of a metal catalyst, via a two-electron redox cycle.2

Detailed investigations into the catalyst activation, nature of active species, factors that govern reactivity and possible deactivation pathways are more difficult to perform in the case of emerging heterogeneous systems such as metal-organic framework (MOF)-supported catalysts,3 for which solution-specific characterization methods are not suitable. Heterogeneous catalysts are notoriously difficult to monitor4,5 and adapted operando methods are highly demanding to achieve a deeper understanding.6

X-ray absorption spectroscopy (XAS) is a powerful element-specific technique for investigating the oxidation state and coordination environment of particular atoms in a material, regardless of the aggregation state of the sample (solid, liquid or gas). The concentration of the investigated element can be as low as a few mM. These properties make XAS an ideal method to obtain detailed information about catalytically active centers supported in solid matrices such as MOFs. Moreover, operando XAS methods provide great opportunities to monitor in real time the structural changes of the catalytic center while avoiding interference from the solid support.7

Constant improvements in the time resolution of XAS methods led to various reactors being designed and adapted to various reaction conditions. In situ/operando XAS measurements became possible in both gas-solid8 and liquid-solid9 reaction systems. In the latter case, Pd nanoparticles supported on active carbon, Al2O3 or polymers were studied by operando XAS for oxidation10 and C–C coupling11 reactions, revealing mechanistic aspects that were inaccessible with other techniques. Surprisingly, catalytic reactions starting from atomic Pd pre-catalysts are less explored, although they could shed light in the debate over the heterogeneity of Pd-catalyzed processes.12

Meanwhile, MOFs evolved to become the most prolific supports in heterogeneous catalysis today, owing to their record-breaking porosity and their unprecedented degree
of tunability, which allow more complex catalysts to be embedded in a controlled manner. Our groups have previously developed MOF-supported Pd catalysts that exhibited excellent reactivity and recyclability for C–C cross-coupling reactions, and for the functionalization of aromatic C–H bonds, which are essential tools for creating new organic molecules. However, preliminary ex situ investigations revealed that despite the apparent recyclability, the catalyst compositions showed obvious differences before and after the reaction. In addition, the same MOF-supported catalysts suffered from an unexplainable rapid deactivation in other reactions (e.g. the Heck coupling). These peculiar observations highlighted the necessity to identify better techniques for studying the behavior of MOF-supported catalysts.

A custom reactor was earlier developed by us for the simultaneous acquisition of operando XAS and powder X-ray diffraction (PXRD) data. This set-up enables the correlation of information about the active catalytic species with the changes in the structural stability of the crystalline solid support. The reactor was designed for operation at synchrotron beamlines. It includes an in-built miniaturized stirring plate and parameters like temperature, pressure as well as the addition of reagents can be controlled remotely. Duplicate experiments under identical conditions were followed by ex situ NMR spectroscopy, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy dispersive spectroscopy (EDS). Combining the information extracted from these methods we have unambiguously probed the entire "lifetime" evolution of the Pd species in Pd(II)@MOF pre-catalysts during the Heck coupling reaction. This "lifetime" includes activation of the pre-catalyst, catalysis driven by different types of active species and deactivation of the catalysts. This information further enabled us to manipulate and prolong the activity of our catalyst.

The method described herein is widely applicable to the study of complex catalytic systems promoted by the majority of supported transition metal complexes, where traditional spectroscopic techniques are not sufficient.

**EXPERIMENTAL SECTION**

**Materials**
Pd(II)@MIL-101-NH₂, Pd(0)@MIL-101-NH₂, Pd(II)@MIL-88B-NH₂ and Pd(0)@MIL-88B-NH₂ (Pd@MOP, all with ca. 7–8 wt% Pd loading) were synthesized according to procedures previously reported. Details of synthesis and characterization are given in Section S1 of the Supporting Information (SI). All reagents and solvents were used as obtained from commercial suppliers without further purification.

**Reactor for operando experiments**

Reactions were carried out in a custom-built reactor (Figure 1) developed at the Christian-Albrechts University (Kiel, Germany) in cooperation with the beamline staff at the P08 beamline, PETRA III, DESY (Hamburg, Germany). The reactor allows the analysis of chemical reactions and crystallographic transformations under solvothermal conditions using synchrotron-based characterization techniques. It consists of an aluminum casing that holds Duran® glass vials with a maximum volume of 6 mL. The inner diameter of the vials used was 10 mm and the thickness of the glass wall was 1.0 mm. The whole reactor was aligned on the beamline in transmission geometry. The aluminum casing was surrounded by a heating mantle made of copper wires. Typically, the reaction mixture was brought to target temperature in less than 1 min. The actual temperature of the reaction mixture was constantly monitored using a PTFE-coated thermocouple and kept close to the target temperature through a combination of resistive heating and direct cooling of the heating mantle with compressed air. To initiate very fast reactions or alter chemical parameters during the reaction, the injection of reagents was triggered remotely via two tubes embedded into the reactor’s cap. The tubes were connected to a neMESYS syringe pump fitted with 5 mL glass syringes. A magnetic stirrer was placed under the base of the aluminum casing to ensure homogeneous distribution of particles in the pathway of the X-ray beam.

**Operando XAS and PXRD experiments**

Operando XAS and PXRD data were collected on the beamline BM01B at the ESRF, Grenoble, France. Detailed descriptions of data collection and analysis are given in Section S2. PXRD data were collected on a Dectala 2D detector using X-rays with an energy of 24.55 keV (λ = 0.505 Å). XAS measurements were performed at the Pd K-edge (24.35 keV) in transmission mode with an energy range from 24.00 to 25.25 keV. During the catalytic reactions XAS and PXRD data were collected in bundles of 5 scans each, alternating between the two modes of the beamline. The acquisition of five XAS spectra required ca. 17 min (3.4 min/scan). The time necessary to switch from XAS to PXRD, collect five diffraction patterns and switch back to XAS was ca. 2.4 min. This sequence was repeated for the entire duration of the experiment, as described in Figure 2.

For PXRD data, minimal changes were observed between the five consecutive frames. Therefore, intensities from the
five frames were summed up in order to improve the intensity statistics. For XAS data, all scans were treated individually as the sample composition changed with time. The data treatment, including pre-edge subtraction, spline removal, normalization and Fourier transformation, was performed with the EXAFSPAK package.\textsuperscript{22} The experimental $k^2$-weighted EXAFS oscillations were analyzed by non-linear least-squares fits of the data to the EXAFS equation, refining the model parameters, number of backscattering atoms ($N$), mean interatomic distances ($R$), Debye-Waller factor coefficients ($\sigma^2$), and threshold energy ($E_o$). The spectrum of a palladium metal foil was recorded simultaneously in transmission mode as reference with the first inflection point of the absorption edge defined as 24.350 keV.\textsuperscript{23} The theoretical phases and amplitudes used in the refinements were calculated using the FEFF7 program.\textsuperscript{24} The standard deviations reported for the refined parameters were obtained from $k^3$ weighted least-squares refinements of the EXAFS function $\chi(k)$, and without including systematic errors. These statistical error values allow reasonable comparisons, \textit{e.g.} of the significance of comparing relative shifts in the distances. However, the variations in the refined parameters, including the shift in the $E_o$ value (with $k = 0$), using different models and data ranges, indicate that the accuracy of the distances given for an individual complex is between ±0.005 and ±0.02 Å for well-defined interactions. The “standard deviations” have been increased accordingly to include estimated additional systematic errors.

**NMR and TEM experiments**

The experiments at the beamline were repeated in the laboratory under identical conditions in order to acquire NMR and TEM data and correlate it with that obtained by XAS. Small aliquots (<50 µL) were taken from the hot reaction mixture at regular intervals, extracted with cold CDCl$_3$ and analyzed by $^1$H NMR spectroscopy to measure conversion. The $^1$H NMR spectra were recorded at 400 MHz on a Bruker Advance spectrometer. Alternatively, a droplet of the aliquot was transferred to a Cu grid without further treatment. The grid was immediately placed into the vacuum chamber of the microscope for TEM and EDS analysis. TEM observations and EDS mapping were performed on a JEOL JEM-2100F microscope equipped with a Schottky field emission gun, and operated at 200 kV. Images were recorded with a Gatan Ultrascan 1000 CCD camera.

**Catalytic reactions under standard conditions**

Aryl iodide (0.1 mmol), olefin (1.3 equiv.), sodium acetate (2 equiv.), and Pd@MOF catalyst (0.003 mmol) were stirred in a mixture of deionized water (0.5 mL) and dimethoxoethane (DME, 1.5 mL) in a vial sealed with a septum-fitted cap. The reactions were performed in air. Minimum reactivity was observed at 60 °C and optimal reactivity was observed at 90 °C. Under these conditions, the catalyst was completely deactivated after one run and could not be recycled. Details about the optimization of reaction parameters and the substrate scope are given in Sections S3 and S4. $p$-Iodobenzonitrile and tert-butyl acrylate were chosen as model substrates for the \textit{operando} experiments (Scheme 1).

![Scheme 1. Model Heck coupling for \textit{operando} experiments.](image-url)

**Catalytic reactions for \textit{operando} experiments**

To achieve XAS data of sufficient quality and a rapid completion of the organic reaction, the total concentration of reactants was doubled and the catalyst loading was further increased to ca. 18 mol%. $p$-Iodobenzonitrile (0.4 mmol), tert-butyl acrylate (1.5 equiv.), NaOAc (2 equiv.), and Pd@MOF catalyst (0.075 mmol) were mixed in H$_2$O (1 mL) and DME (3 mL) in 6 mL vials. Full conversion was typically achieved within 1 h. At higher overall concentrations, an increased viscosity of the reaction medium impeded stirring. Control experiments confirmed that besides an increased reaction rate, no further differences were observed compared to those under standard conditions. Therefore, the conclusions derived from \textit{operando} studies can be considered relevant for general catalytic experiments.

The following sequence of operations was used as illustrated in Figure 2: \textbf{1.} (t < 0 min): $p$-Iodobenzonitrile (0.4 mmol, 91 mg), sodium acetate (2 equiv., 66 mg) and Pd@MOF catalyst (0.075 mmol, ca. 100 mg for 8 wt% Pd loading in MOF) together with H$_2$O (1 mL) and DME (2 mL) were added to the reaction cell. XAS and PXRD data acquisition was already initiated while the mixture was allowed to stir to homogenize for 10–20 min. \textbf{2.} (t = 0 min): tert-butyl acrylate (1.5 equiv.) was injected with the remaining solvent (DME, 1 mL) and 1 mL headspace gas was simultaneously extracted to avoid overpressure. \textbf{3.} (t = 0–10 min): the temperature was increased to 60 °C in less than 1 min and held constant for 10 min. \textbf{4.} (t = 10–30 min): the temperature was further increased by 10 °C every 10 min up to 90 °C. \textbf{5.} (t = 30–90 min): the temperature was maintained constant at 90 °C for 60 min to achieve completion of the organic reaction. \textbf{6.} (t > 90 min): the mixture was cooled down gradually to room temperature (RT) during which the XAS and PXRD data acquisition was continued.

**Results and discussion**

\textbf{1. Catalytic activity (NMR Spectroscopy)}

Kinetic profiles of the Heck reaction using Pd(II)@MIL-101-NH$_2$ as pre-catalyst are presented in Figure 3a, where both conversion and temperature are plotted as a function of time. Intriguingly, after an initial short period of rapid conversion at 60 °C, a plateau was reached at ca. 70–80 °C (20–30 min after olefin addition) with a clearly diminished activity (Figure 3a, solid blue line). Upon further heating, the rate increased again and the reaction reached completion in ca. 60–70 min. This unusual behavior is indicative of different mechanisms being dominant under different reaction conditions. At the attempt to isolate a single operating mode, we performed additional experiments maintaining the temperature constant at 60 °C. To our surprise, the reaction stopped after only one turnover (Figure 3a, dashed blue line).
Due to the acquisition of the oligomers, the stepwise heating process of 30°C to 25°C is started. This suggests a completely homogenized suspension. In this way, there is a higher probability that the Pd–N mean distance decreased from 2.114(8) Å (Pd coordinated to Ar–NH₂ in the MOF) to 1.993(9) Å (Pd coordinated to R–CN and/or C ligands) at 47 min (vide infra, Table 1). Without the nitrogen donor, Pd species did not have the necessary electron density to perform a second oxidative addition. Furthermore, these Pd species became mobile and could agglomerate into clusters and further into nanoparticles. Therefore, the plateau observed during the stepwise heating process (ca. 20–30 min, Figure 3a, solid blue line) is likely due to the decreased amount of mononuclear Pd complexes coordinated to the MOF linker while the mobile Pd species are unreactive at low temperature (below 90°C). We anticipated that in order to catalyze the reaction at 60°C, Pd might need to coordinate to a more electron rich ligand (such as Ar–NH₂). This was confirmed by adding aniline in stoichiometric amounts to Pd into the reaction mixture. Aniline represents a small homogenized model for the MOF linker that can simulate the same coordination mode. Under these conditions, oxidative addition is faster than aggregation, and full conversion was achieved at 60°C (Figure 3a, dotted blue line). The shape of the reaction profile suggests a completely homogeneous reaction. This is also confirmed by TEM and EDS studies at various stages of the catalytic reaction; no Pd nanoparticles were observed before the completion of the catalytic reaction (Figures S1-2, Section S5).

To establish the generality of this behavior, we also tested Pd(II)@MIL-88B-NH₂, and found that it operates through a related mechanism, with subtle but important differences (Figure 3b, Figure S3, Section S6). When the catalyst was tested at 60°C, the first turnover occurred at a high rate, as in the case of Pd(II)@MIL-101-NH₂. Afterwards the reaction continued, although at a slower rate, instead of being completely suppressed as for Pd(II)@MIL-101-NH₂ (dashed blue line). When using the stepwise temperature ramp to 90°C, a similar behavior as for Pd(II)@MIL-101-NH₂ was observed (solid green line), but the reactivity plateau was less pronounced. We have previously shown that Pd(II) in MIL-88B-NH₂ is coordinated by two amino ligands in a chelating fashion, not only one as in the case of MIL-101-NH₂. In this way, there is a higher probability that Pd remains partly coordinated to amino donors in the MOF, even after the first turnover and does not agglomerate as fast as in MIL-101-NH₂. Thus, although the activity was diminished, this effect was not as drastic as for Pd(II)@MIL-101-NH₂. Furthermore, a sustained activity due to coordination to the second MOF linker is
also in agreement with literature reports showing that bipyridine-type and other chelating ligands could catalyze the Heck coupling reaction more efficiently. It is worth mentioning that the kinetic profiles for Pd(II)@MIL-101-NH₂ and Pd(II)@MIL-88-NH₃ at the early stage (up to 15 min) of the reaction have almost perfect overlap (Figure S4, Section S6). This indicates that the reaction mechanism was the same for both materials at this early stage, and the first catalytic turnover occurred inside the pores.

Importantly, when the reaction mixture was heated to 90 °C, the reactivity was restored for both catalysts (Figures 3a-3b). This indicates that as-synthesized Pd centers may have changed their coordination environment to form mobile mononuclear Pd complexes and Pd clusters or nanoparticles under the reaction conditions, which altered the reactivity of the catalysts at 90 °C. We anticipate that such drastic changes in the Pd coordination environment should be reflected in the XAS spectra. Indeed, the operando XAS monitoring of the Heck reaction revealed previously unseen details, which support a dynamic, adaptive behavior of Pd centers upon exposure to physical and chemical stimuli in the reaction mixture. The XAS data is presented in the following section.

2. Nature of the active species and catalyst deactivation (X-ray absorption spectroscopy)

X-ray absorption spectroscopy (XAS) revealed that clear changes at the Pd centers occurred as soon as the catalyst was added to the reaction mixture. Both XANES and Fourier transformed (FT) EXAFS of as-synthesized Pd(II)@MIL-101-NH₂ with the formula [Pd(Ar-NH₂)(CH₃CN)Cl]₂ are markedly different from those recorded in the first operando XAS scan (Figures 4 and 5, Figures S5a-b, Section S7). Even though the Heck reaction had not yet started, anionic Cl⁻ ligands were already replaced by neutral N-ligands, presumably p-iodosobenzonitrile, which form more stable complexes by several orders of magnitude with Pd(II) in aqueous media (details can be found in Section S2).

We found that the Pd(II) in the resulting cationic complex was rapidly reduced upon olefin addition, in a Wacker-type process. This was proved by carrying out the oxidation of the olefin using Pd(II)@MIL-101-NH₂ (30 mol% Pd) under the same XAS reaction conditions. Despite the low stability of the resulting α-formylacetate derivative in basic media and high temperature, we were able to observe characteristic aldehyde signals (9.9-9.6 ppm) in the ¹H NMR spectrum (Figure S6, Section S8). This process required both olefin and water (Figure S7, Section S8). In the absence of H₂O, Pd remained in oxidation state +II, even upon heating to 60 °C, and was homogeneously distributed in the MOF crystals as indicated from the TEM images (Figure S7a, Section S8). The in situ generated atomic Pd(0) triggers the Heck coupling, being re-oxidized by the aryl iodide substrate in the initial oxidative addition step of the catalytic cycle (vide infra, Figure 8).

The XANES features of as-synthesized Pd(II)@MIL-101-NH₂ and their evolution as a function of time under Heck conditions is presented in Figure 5. The overview of all XANES spectra recorded during one operando experiment (as described in Figure 2) is shown in Figure 4a. The XANES spectra have the same edge features appeared as one smooth peak at the beginning of the measurement. Then the smooth peak gradually split into two smaller peaks. This overview indicates an initial stable state and thereafter a transformation stage of Pd species during the measurement.

To follow the changes in detail, representative XANES spectra were selected and compared with as-synthesized Pd(II)@MIL-101-NH₂ and a metallic Pd foil reference (Figures 4b and 4c). Figure 4b focuses on the initial stages of the reaction. It is noted that the first XANES spectrum recorded under operando measurement condition shows significant changes compared with the XANES spectrum of the as-synthesized Pd(II)@MIL-101-NH₂ (Figure 4b, green line). This reveals the changes of the coordination environment of Pd atoms when the as-synthesized catalyst was added into the reaction mixture. From the start of the operando data acquisition until the reaction temperature reached 80 °C, the XANES spectra overlap and show almost identical edges at 24354 eV and similar profiles after the edge. This indicates that the observed Pd species have a similar coordination environment from the start of the operando measurement at RT to 80 °C. During this period, edge positions are located close to the as-synthesized Pd(II)@MIL-101-NH₂ and about 4 eV above the Pd metal foil reference, which has the oxidation state zero and K-edge position at 24350 eV. Considering that a one-step change in oxidation number commonly introduces a K-edge shift to a higher energy by 2.0 to 2.5 eV, these results confirm that Pd mainly maintained an oxidation state of +II during this reaction period. These observations are in agreement with the NMR data (vide supra). We can conclude that the freshly reduced Pd(0) was short-lived and reacted immediately upon heating to 60 °C. It is thus reasonable that at sufficiently high concentration of aryl iodide, Pd is re-oxidized much faster than the time resolution of the present XAS experiments (ca. 3.4 min/scan). A cationic resting state as a Pd(II) complex during the catalytic cycle is likely to be the one observed by XAS, thus not showing major differences from the pre-catalyst. Figure 4c includes selected XANES spectra of Pd(II)@MIL-101-NH₂ covering the entire experiment. The spectrum of the recycled catalyst and that of the Pd foil are also included. When the spectra were observed compared to those recorded at
Figure 4. Normalized Pd K-edge XANES spectra of Pd(II)@MIL-101-NH$_2$ catalyst as a function of measurement time. (a) All XANES spectra displayed in three-dimensions. (b) Selected XANES spectra showing the as-synthesized Pd(II)@MIL-101-NH$_2$, the heating steps and Pd reference. (c) Selected XANES spectra at RT, 90 °C, cooling back to RT, recycled and Pd reference.

The composition of Pd species during this transformation and their corresponding ratios were studied by linear combination fit (LCF) of the XANES spectra. Detailed LCF fit and analysis are described in Figure S8 and Section S9. The fairly good fit results confirm that the catalysis system consisted of mononuclear Pd(II) complexes and Pd(0) nanoclusters. The fractions of different Pd components during the operando experiment are displayed in Figure 6. At the start of the operando measurement, the catalyst consisted of 100% mononuclear Pd(II) complexes and 0% nanoclusters. The complexes started transforming into nanoclusters from 31 min when the temperature reached 90 °C. Generally, the rate of transformation was high at the beginning, appearing as steep slopes and then decreased. The transformation reached completion in the recycled catalyst where only Pd(0) nanoclusters were present.

Figure 5. Fourier transformed $k^3$-weighted EXAFS data as a function of time showing the coordination environment of Pd in Pd(II)@MIL-101-NH$_2$. The spectra are not phase corrected. * The peak at ca. 1.9 Å comprises the signal of Pd–Cl single scattering and the side peak of Pd–Pd single scattering.

System was heated to 90 °C, changes in the XANES shifted towards a lower energy. These changes became even more pronounced for the recycled catalyst. Its edge position further shifted to 24352 eV indicating the presence of Pd in both metallic Pd(0) and oxidized Pd(+II) forms. These observations suggest a gradual increase in the degree of transformation of mononuclear Pd(II) complexes into Pd(0) nanoclusters, and part of the Pd atoms in recycled catalyst remained in an oxidized form.

Figure 6. Fractions of mononuclear Pd(II) complexes and Pd(0) nanoclusters in the catalyst derived from the linear combination fit of the XANES spectra.

The specific coordination environment of Pd atoms in the MOF was further investigated by analyzing the corresponding FT EXAFS spectra from the same operando experiment.
(Figure 5). The FT spectrum of the as-synthesized Pd(II)@MIL-101-NH₂ is shown in Figure 5 (22 min) which contains two major peaks corresponding to the Pd–N and Pd–Cl bonds. Refinement of the data suggests a formula [Pd(ArNH₂)(CH₂CN)Cl]₂. During the first part of the operando measurement, the temperature of the reaction system was increased from RT to 90 °C (up to 31 min) and the FT spectra were very similar with only one major peak corresponding to Pd–N/C bonds with an average coordination number of 4. The Pd–Cl bonds disappeared immediately when the as-synthesized catalyst was added into the reaction mixture. This indicates that the initial Pd complex containing Pd(II)–Cl bonds did not participate in the catalytic process. EXAFS spectra recorded at 24 min (at 80 °C) and 34–38 min (at 90 °C) are excluded because of the unreatachable data quality (this phenomenon is discussed in Section S2). Interestingly, after the temperature was stabilized at 90 °C, the EXAFS data quality was quickly recovered. At this stage (at 31 min), a peak corresponding to Pd–Pd bonds appeared and later became clearly visible with increasing intensity. Importantly, as the Pd–Pd peak became more prominent, a Pd–Cl peak also emerged, while the Pd–N/C peak decreased in intensity. The formation of Pd–Cl bonds indicates the presence of Pd(II) in the system, which is caused by oxidation of Pd atoms on the surface of nanoclusters, as later confirmed by EXAFS refinement. It should be noted that the shoulder side peak of Pd–Pd bond in the Fourier transform is at about the same position of the peak corresponding to Pd(II)–Cl bond. A thorough EXAFS data analysis proving the existence of Pd–Cl bonds can be found in Figures S9–S12 and Section S10. In addition to the confirmation from EXAFS data, inductively-coupled plasma atomic-emission spectroscopy (ICP-OES) was used to determine the element composition of the recycled catalyst. The results showed that significant amount of chloride (1.05 wt%) remained in the recycled catalyst. The molar ratio of Pd/Cl derived from ICP-OES results is ca. 1.2. This is in good agreement with the result from the EXAFS refinement (Table 1) which implies that each Pd atom was bound to one Cl⁻ ion on average. These observations from FT spectra are consistent with the information obtained from XANES spectra suggesting the formation of mononuclear Pd(II) complexes from the as-synthesized catalyst followed by the continuous transformation of mononuclear Pd(II) complexes into Pd(0) nanoclusters when the reaction system was heated to 90 °C. The existence of Pd–Cl also explains the oxidation state of Pd in the recycled catalyst determined by its K-edge position.

Local structures of the Pd atoms during the operando measurement were determined by fitting of the EXAFS spectra corresponding to the FTs in Figure 5. A maximum of three shells of Pd–Pd, one shell of Pd–N/C and one shell of Pd–Cl distances were introduced to optimize the EXAFS fitting. FT spectra of Na₂PdCl₄ and Pd metal foil were used as references to confirm the Pd–Cl and Pd–Pd bonds in our system. The model for fitting Pd–Pd was the crystalline structure of metallic palladium, with face-centered cubic packing. The experimental EXAFS spectra and their best fits are shown in Figures S5, Section S7. The final fitting parameters are given in Table 1. The average size (i.e. average number of Pd atoms) of the Pd clusters was estimated from the coordination numbers (CN) of Pd–Pd in the first shell refined from the EXAFS data. It shall be noticed that the CN values determined from EXAFS refinements are average values without taking into account of the fraction of each Pd species. The true CN values for Pd–Pd equal to the CN values from EXAFS refinement divided by the corresponding fractions of the Pd nanoclusters. It shall be stressed that the Pd nanoclusters transformed from mononuclear Pd complexes are on average smaller than 1 nm in size and each cluster consists of ca. 13 Pd atoms. They are considerably smaller than the nanoparticles in commercial catalysts, such as Pd@C,[11,12] Pd@Al₂O₃[8,10,32] and Pd@polymers.[13] Meanwhile, the mean Pd–Pd bond distances in the Pd nanoclusters were also determined from EXAFS refinements (Table 1), and they are between 2.65 – 2.67 Å. Interestingly, these bond distances are significantly shorter than the distances found in Pd foil (2.74 Å) and Pd nanoparticles with size of ca. 2 nm (≥ 2.71 Å).[10,11] It is known that Pd atoms on the surface of Pd nanoparticles form shorter Pd–Pd bonds compared with Pd atoms at interior due to lower coordination number of the surface atoms. The average bond distances of Pd–Pd and their corresponding particle sizes had also been investigated by an accurate all-electron density functional approach. These previous studies strongly support the Pd nanoclusters model we proposed here including the bond distance and average nanocluster size. With an average cluster size of ca. 13 atoms, most of the Pd atoms are on the surface of the nanoclusters. Therefore, such small Pd nanoclusters should still be highly catalytically active, judged by size alone[33] and by the number of Pd atoms with coordination sites available. However, the rise of the Pd–Cl peak in the Fourier transforms offers a first hint into the real motive behind the catalyst deactivation.
Table 1. Refined distances (d/Å), and mean number of distances (N) in selected scans using the Pd(II)@MIL-101-NH₂ catalyst.

| Catalyst          | d(Pd-N/C) (Å) | CN | d(Pd-Cl) (Å) | CN | d(Pd···Pd) 1st | CN | d(Pd···Pd) 2nd | CN | d(Pd···Pd) 3rd shell | CN |
|-------------------|---------------|----|---------------|----|---------------|----|---------------|----|----------------------|----|
| As synth.         | 2.114(8)      | 2.0| 2.298(1)      | 2.0|               |     |               |     |                      |    |
| First scan        | 2.083(6)      | 4.0|               |    |               |     |               |     |                      |    |
| 31 min            | 2.056(4)      | 3.8|               |    |               |     |               |     |                      |    |
| 44 min            | 2.037(6)      | 3.4|               |    |               |     |               |     |                      |    |
| 47 min            | 1.993(9)      | 2.9|               |    |               |     |               |     |                      |    |
| 50 min            | 2.026(8)      | 2.8|               |    |               |     |               |     |                      |    |
| 57 min            | 1.980(6)      | 1.3| 2.37(1)       | 0.4| 2.654(4)      | 2.85(5.6)| 3.76(2)      | 1.0| 4.68(2)             | 2.0|
| 63 min            | 1.956(5)      | 1.0| 2.35(1)       | 0.7| 2.653(4)      | 3.15(5.6)| 3.74(4)      | 1.0| 4.73(2)             | 2.0|
| 73 min            | 1.979(7)      | 0.8| 2.38(2)       | 1.0| 2.662(3)      | 3.24(9)| 3.76(1)      | 1.0| 4.73(2)             | 2.0|
| 85 min            | 1.959(7)      | 0.9| 2.38(1)       | 1.0| 2.662(3)      | 3.74(9)| 3.78(2)      | 1.0| 4.75(1)             | 2.0|
| 115 min           | 1.978(7)      | 0.8| 2.38(4)       | 1.0| 2.662(2)      | 4.21(5.3)| 3.76(2)     | 2.0| 4.85(1)             | 3.0|
| Recycled          | 2.415(3)      | 1.0|               |    | 2.689(1)      | 6.5 | 3.815(6)     | 3.0| 4.747(3)            | 6.0|
| Pd foil           |               |    | 2.741(1)      | 12.0| 3.904(8)     | 6.0 | 4.767(2)     | 24.0|

aThe standard deviations in parentheses were obtained from k³-weighted least square refinements of the EXAFS function χ(k) and do not include systematic errors of the measurement. bThe estimated error of the coordination is ca. 25% of the given value when refined. Underscored parameters have been optimized and fixed in the refinements. cThe CN values in parentheses are the true coordination numbers of Pd–Pd 1st shell when the fractions of Pd nanoclusters were taken into account. These values were used to determine the average size of Pd nanoclusters. dThe bond distance and CN value of Pd–Pd 1st shell at 31 min contain relatively big errors because of the weak EXAFS signal when Pd nanoclusters just started to form.

Figure 7. Proposed Pd species at different stages during the Heck coupling reaction using Pd(II)@MIL-101-NH₂ as a catalyst. The red trace shows the temperature and the blue trace shows conversion to the desired product. The value of CN in the figure refers to the coordination number of Pd–Pd in the first shell.
The average coordination number of Pd–N/C maintained at 4.0 when there was no transformation of Pd(II) species. As the mononuclear Pd(II) started to reconstruct into Pd(0) nanoclusters, the average CN of Pd–N/C decreased to ca. 3.4 at 44 min and to ca. 0.8 at 115 min indicating a continuous transformation process. The first Pd–Cl bonds were observed after 57 min with an average CN of ca. 0.4. The reaction conversion had at this time already reached ca. 95% (Figure 3a). The average CN then further increased and ended up at ca. 1.0. It shall be noted that the bond distances of the reformed Pd–Cl bonds were 2.35–2.42 Å, which is significantly longer than those in Pd(II) complexes. This indicates that the Pd atoms coordinated to Cl were surface atoms of the Pd nanoclusters, where each Pd atom bound to several Pd atoms and the Pd–Cl bonds became longer in comparison with Pd(II) complexes. This also indicates that when Cl ions are coordinated to the relatively bulky and less mobile Pd nanoclusters, they could not easily be replaced by the amino groups of the MOF linkers. In addition, no EXAFS signals corresponding to Pd–Cl–Cl and Pd–Cl–Pd–Cl multiple scattering paths were observed, which excludes the presence of PdCl₂. Furthermore, no EXAFS signal corresponding to Pd–O single scattering was observed in the recycled catalyst, which suggests that surface Pd of the nanoclusters were coordinated to Cl ions. Otherwise, they would have been oxidized in air to form Pd–O bonds. The recycled Pd(II)@MIL-101-NH₂ was measured by ex situ EXAFS (Figure S5f, Section S7). No EXAFS signal from Pd–N/C distances was found from the refinement and average coordination numbers of Pd–Pd and Pd–Cl bonds were determined to be ca. 6.5 and ca. 1.0, respectively. The Pd–Pd bond distance is longer (ca. 2.69 Å) than Pd–Pd bond distances (2.65 – 2.67 Å) during operando measurement (44 – 115 min) indicating larger clusters, but still shorter than the Pd–Pd distance of a 2 nm Pd nanoparticle. It is reasonable to propose that at this stage of the process, Pd nanoclusters became the absolute dominating species with an average size of ca. 20 atoms, and the surfaces of these Pd nanoclusters were almost covered by Cl ions leading to the deactivation of the catalyst. It shall be noted that the coordination numbers and the estimated sizes of Pd clusters obtained from the EXAFS fitting are an average of various Pd species. In reality, it is likely that both larger Pd nanoparticles with higher coordination numbers and smaller Pd clusters with lower coordination numbers coexist in the sample. Based on the operando XANES and EXAFS analyses, the evolution of Pd species was followed and the catalytically active species under Heck conditions were identified. The kinetic profile (vide supra) of the identified Pd species are illustrated in Figure 7. The active species were mononuclear Pd(II) complexes coordinating to the linkers of the MOF at the beginning of the reaction below 90 °C. The mononuclear Pd(II) complexes then dissociated from the linkers after one run and their activity was lost when the temperature was raised and maintained at 90 °C. As the temperature was raised and maintained at 90 °C, these mobile mononuclear Pd(II) complexes gradually converted to Pd nanoclusters of ca. 13 Pd atoms on average. A mixture of the mobile mononuclear Pd(II) complexes and Pd nanoclusters co-existed and became the active species to catalyze the reaction. The activity of the mobile mononuclear Pd complexes at 90 °C was confirmed by adding a second load of reagents at 70 min, when the system consisted of ca. 40% mononuclear Pd complexes and 60% Pd nanoclusters covered and poisoned by coordinated
Cl− ions (Figure 7). A full conversion of the new reagents was achieved in another 70 min at 90 °C. This experimental result proved that the mobile Pd mononuclear complexes are catalytically active after the reaction system was heated to 90 °C during the *operando* measurement. At the beginning of this stage, mononuclear Pd complexes appeared also as the major Pd species compared to the Pd nanocluster. The mononuclear Pd complexes have even better activity than the corresponding Pd nanoclusters considering the size and the number of coordination sites available. This continuous conversion of the Pd species also indicated that mononuclear Pd complexes had a relatively high activity because it could compete with the aggregation process under the reducing conditions. After Cl− ions were bound to the surface of the Pd nanoclusters, the remaining mononuclear Pd(II) complexes catalyzed the reaction to its completion. When the substrates were completely consumed, mononuclear Pd complexes could not react and they self-aggregated into Pd nanoclusters, which were quickly poisoned by remaining Cl− ions in the system. A similar evolution of Pd species was also observed from Pd(II)@MIL-88B-NH2 catalyzed reaction. The corresponding XANES and EXAFS spectra can be found in Figure S13, Section S11.

A mechanism derived from the above-described investigations is proposed and shown in Figure 8. The freshly produced Pd(0) complex (I) represents the active species that initiate the catalytic cycle by oxidative addition in the C–I bond, leading to the Pd(L2)ArI intermediate (II). The absence of any Pd–I distances in the EXAFS data is not surprising. The oxidative addition is rapidly followed by a ligand exchange reforming the favored cationic species stabilized by a neutral N-ligand, following a similar preference as observed in the early stages of the experiment. This leads to an intermediate complex (III), to which the olefin coordinates to form a π-complex (IV). Intermediates III and IV contain solely Pd–C/N bonds, in agreement with the XAS data. Based on this analysis, it is reasonable to conclude that the resting state of Pd species observed by XAS in the early stages of the measurement corresponds to intermediate IV, in which Pd has an oxidation state of +II. This is also in agreement with numerous reports that pointed out the migratory insertion step to be turnover-limiting. In the following step, a β-hydride elimination yields the final organic product and a palladium hydride species (VI) that upon reductive deprotonation returns to Pd(0), completing this cycle.

### 3. Framework stability and catalyst distribution inside the MOFs (TEM, EDS, PXRD)

Duplicate experiments were recreated as described in Figure 2 and monitored by TEM and STEM/EDS. The distribution of Pd in MIL-101-NH2 crystals was investigated at various stages during the Heck coupling reaction (Figure 9). To minimize possible Pd aggregation introduced during the TEM sample preparation, a droplet of the hot reaction mixture was directly deposited onto the TEM grid and transferred into the vacuum chamber of the microscope. At the initial stage, no Pd nanoparticles were visible in the TEM images, both inside and outside MIL-101-NH2 crystals (Figure 9a). In addition, EDS mapping showed the presence of homogenously distributed Pd throughout the framework (Figure 9b). This confirms that the pre-catalyst consisted of Pd(II) complexes, embedded inside the MIL-101-NH2. After the Heck reaction was initiated, TEM images recorded at various stages of the reaction (25%, 54% and > 99% conversion) showed formation of Pd nanoparticles of 2–15 nm in size on the surfaces of the crystals (Figures 9a2 - 9a4). The presence of the Pd nanoparticles shown in Figure 9a2 (25% conversion at 70 °C) was probably caused by transformation of Pd complexes into Pd nanoclusters during the rapid cooling and interruption of the catalytic process. Considering the significantly smaller average size of Pd species derived from EXAFS (Table 1), the presence of such large Pd nanoparticles is partially due to the promoted aggregation of the Pd nanoclusters transformed from resting Pd complexes especially under the condition of solvent evaporation. The large particle size also implies that much smaller Pd clusters should also be present in the MOF crystals. Indeed, the small Pd clusters and mononuclear Pd complexes were captured by EDS mapping which showed clear Pd signals within the entire MOF particles (Figures 9b1 - 9b3). The EDS spectra also confirmed that Pd species remained inside the MOF crystals at all stages of the reaction, although the Pd/Cr ratio gradually decreased with time (Figures S14-S15, Section S12).

![Figure 9. TEM images (a) and STEM image and EDS mapping (b) of Pd(II)@MIL-101-NH2 at various stages during the Heck reaction: at 0% (a1-b1), 25% (a2-b2), 54% (a3-b3) and > 99% (a4-b4) conversion.](image-url)

The lack of recyclability of the MOF under the Heck coupling conditions indicates that not only the possible large Pd nanoparticles observed outside the MOF crystals by TEM, but also the small Pd species within the MOF crystals were already inert. This information is extremely important as it proves that it was neither the Pd leaching nor the Pd aggregation itself that led to the deactivation of the catalyst. Instead, the deactivation was caused by the poisoning of Cl− ions. Furthermore, the *operando* PXRD data proves that both MIL-101-NH2 and MIL-88B-NH2 were completely stable and no structural changes occurred under these reac-
tion conditions (Figure S16, Section S13). Based on all information acquired, a clear picture emerges. The deactivation of the catalyst is not of a physical nature. Different from the structural degradation factors commonly suggested in the literature such as Pd leaching and agglomeration or MOF decomposition, the predominant deactivation pathway here is of a chemical nature. The irreversible capping of small Pd clusters with chloride ligands makes the reactive sites inaccessible to the reaction partners, long before Pd leaching or aggregation becomes a major issue.

4. Recyclability

With the above information in hand, we revisited the issue of recyclability. Initial studies showed a dramatic loss of activity in the second cycle, after the catalyst was recovered, washed and dried. However, when fresh reagents were added during the reaction phase of high activity, before a complete inhibition by Cl⁻ ions was achieved, a high TOF could be maintained for at least 3 cycles. Despite the disturbance introduced by fresh reagents (temperature, solubility, reagent ratios) the reaction was faster than what would have been necessary to convert three batches of starting materials by fresh catalysts (Section S14). This experiment was purely illustrative and does not represent a practical experimental procedure. However, it suggests that operation under continuous flow would be a suitable way to improve the total turnover of the catalyst. Cl⁻ ions could be washed away at the beginning of the experiment and a constant feed of fresh reagents would postpone the deactivation process.

Even though the recyclability of the material did not work as expected, we observed remarkable differences when comparing the activity of the Pd(II)@MOF with its homogeneous counterparts. When the reaction was performed using the same palladium precursors (i.e. Na₂PdCl₄ and PdCl₂(MeCN)₂) as catalysts without being impregnated into the MOF support, the yields dropped to 42-43% for both Pd(II) salts. This clearly shows the beneficial effect of the MOF support in this catalysis.

5. Discussion

The correlation of data from multiple characterization techniques portrays Pd@MIL-101-NH₂ and Pd@MIL-88B-NH₂ as heterotopic multifaceted catalysts with more than one mode of action. In their as-synthesized dry form, both Pd(II)@MOF pre-catalysts contain Pd centers in a +II oxidation state and square planar coordination geometry, bearing two anionic Cl⁻ ligands. When the catalyst was mixed with the other reagents except for olefin, the chloride ligands were immediately released and replaced by neutral nitrogen ligands, forming a cationic complex favored by the polar aqueous environment. Upon olefin addition in the presence of water, Pd(II) was rapidly reduced to Pd(0) even at room temperature. The freshly reduced Pd underwent a fast oxidative addition, initiating the catalytic cycle. The Heck coupling product was already detectable immediately after reaching 60 °C, proving that mononuclear Pd(II) complexes attaching to the linkers of the MOFs were competent active species to catalyze this transformation at relatively low temperatures.

The first catalytic turnovers have taken place inside the MOF pores, and proceeded with comparable rate for both Pd@MIL-101-NH₂ and Pd@MIL-88B-NH₂ catalysts. During the first cycle, the coordination to the amino-terephthalate linker was lost in the case of MIL-101-NH₂, leading to the formation of an even more electron-deficient Pd species, which could travel through the pores. A second oxidative addition could not be initiated by this form of electrophilic Pd, which instead gradually agglomerated into small nanoclusters. The resulting mixture of the mobile mononuclear Pd complexes and the Pd nanoclusters was inert at 60 °C, and became active in the catalytic cycle at 90 °C. However, upon depletion of the starting materials and further upon cooling the reaction mixture, the surface of the Pd clusters was covered by Cl⁻ ions and their catalytic properties were finally lost. Similar conclusions can be derived for Pd(II)@MIL-88B-NH₂ although the chelating coordination mode of the MOF and the more confined pore space attenuated the deactivation process.

This study fits into a larger effort to bring a better understanding to the complex behavior of palladium under reaction conditions specific for C–C and C–heteroatom bond formation. In recent years, it has become evident that the actual landscape of active species is more diverse and dynamic than previously believed. Starting from mononuclear Pd catalysts, formation of Pd clusters is often unavoidable. However, these particulate species not only represent an alternative resting state for Pd but can also get involved directly in the second stage of catalysis. The presence of rapidly inter-convertible species that possess different levels of reactivity makes it challenging to quantify precisely their contribution to the total observed catalytic effect. Moreover, commonly employed heterogeneity tests may not always provide reliable results. Without a better understanding of these phenomena, a rational design of superior catalysts would not be achievable.

Towards this goal, the method presented herein can reveal fine details of the reaction mechanism by monitoring more precisely the evolution of different Pd species and the effects of Pd phase transitions on its catalytic activity. Moreover, we are continuously working to expand the applicability of the method. Further development of the in situ reactor will make the acquisition of fluorescence XAS data in operando mode feasible. This would be especially beneficial to measure highly diluted samples or catalysts with relatively low absorption edge energies. Furthermore, the new generation of synchrotron radiation sources will provide great opportunities to improve the time resolution and investigate reactions with significantly shorter half-lifetimes.

Conclusions

The mechanism of a Pd@MOF-catalyzed Heck C–C coupling reaction was investigated in detail using a newly developed reaction cell suitable for operando studies of heterogeneous catalysts. For the first time we probed the entire lifetime of the catalyst and revealed fine details of the reaction mechanism that would otherwise remain hidden. Different active species operating at different reaction stages and under different reaction conditions have been identified, together
with their activation and deactivation pathways. The irreversible deactivation of the catalyst was provoked neither by leaching of the active species, nor by decomposition of the crystalline framework. Instead a chemical deactivation mechanism was identified, in which Cl ions cover the surface of transformed Pd clusters and nanoparticles, blocking the access of starting materials to the active sites. This information can be used to prolong the lifetime of the catalytic converter and to design improved catalysts and processes in the future. Importantly, the method described is widely applicable to study diverse chemical reactions catalyzed by transition metals, including both homogeneous and heterogeneous systems, and has the potential to provide unprecedented insight into the fine details of the mechanism. Other complex mechanisms of MOF-catalyzed processes are currently under investigation in our laboratories.

ASSOCIATED CONTENT

Supporting Information
Catalysts synthesis; optimization of reaction conditions, substrate scope and recycling experiments; additional studies of kinetic profiles by 1H NMR; details on the XAS and PXRD data collection; XAS data treatment and refinement results; additional TEM and EDS results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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