# Structure Evolution of Single-Site Pt in Metal-Organic Framework

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Dedicated to Prof. Patricia A. Thiel

## ABSTRACT

Heterogeneous single-metal-site catalysts or single-atom catalysts research has grown rapidly due to the accessibility of modern characterization techniques that can provide invaluable information at the atomic-scale. Herein, we study the structural evolution of isolated single Pt sites incorporated in a metal-organic framework containing bipyridine functional groups using in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with CO as the probe molecule. The structure and electronic properties of the isolated Pt sites are further corroborated by X-Ray Photoelectron Spectroscopy (XPS), aberration-corrected scanning transmission electron microscopy (AC-STEM). We find the prerequisite of high temperature He treatment for Pt activation and CO insertion and inquire into the structural transformation of Pt site process by using dynamic nuclear polarization (DNP)-enhanced solid-state nuclear magnetic resonance (SSNMR) spectroscopy.

#### **INTRODUCTION**

Studies of heterogeneous catalysts for the production of clean energy have increased rapidly over the years. Single-atom catalysts (SACs) with atomic-scale precision, consisting of single metal atoms stabilized on high surface area materials including metal oxides, zeolites, metal-organic frameworks (MOFs), and carbon-based nanostructures, have demonstrated promising catalytic performance for hydrogen production, CO<sub>2</sub> reduction, and solar energy conversion.<sup>1-6</sup> SACs have shown the highest atomic utilization efficiency in catalysis.7-11 Among various support materials, MOFs, constructed from organic linker and inorganic secondary building units, have become an emerging platform for the heterogeneous SACs due to their well-defined pore geometry, tunable pore sizes, large porosity, high surface areas, and versatile chemical functionalities.<sup>9-11</sup> By carefully choosing MOFs of proper structure and functionalities, it is possible to produce relatively uniform and isolated active sites.<sup>12-15</sup> For example, Lin et al. developed single-atom catalysts using N-containing organic linkers to stabilize transition metal active sites, such as Ru, Re, Ir, Pd, Co, and Fe, for various organic transformation reactions.<sup>16-20</sup> Other research groups also demonstrated that isolated single Pt atoms on similar Ncontaining MOFs are promising catalysts for photocatalytic hydrogen production from water.<sup>3,21,22</sup> To understand the origins of these novel catalytic properties and the stability of SACs, extensive characterizations of the coordination structure of single-atom metal sites with atomic-scale precision are indispensable. Such studies are also crucial for the rational design of improved SACs.<sup>21,23-26</sup>

Owing to recent instrumentation advancements, aberration-corrected scanning transmission electron microscopy (AC-STEM), which can distinguish and locate the position of isolated single metal atoms, has emerged as a powerful tool for directly interrogating isolated metal atoms in SACs.<sup>27, 28</sup> However, the 'exclusive' presence of single-atom sites drawn from AC-STEM images provides statistically limited information, because the observation is restricted to a tiny portion of the samples due to practical reasons.<sup>29</sup> Besides, AC-STEM does not provide information relating to coordination structures of single-atom sites. Infrared spectroscopy with CO being probe molecule has been widely used as the approach to characterize the metal surface and distinguish different metal sites, especially SACs and metal nanopartiles.<sup>24, 30</sup>

Herein, we synthesize isolated Pt single atoms supported on N-containing MOFs (Pt@MOF-253). Using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with CO as the probe molecule, we study the structural evolution of Pt sites in MOF-253 with thermal treatments under inert and reductive gas environments. We perceive the critical role of He treatment on Pt activation for CO coordination. To have a deep understanding of the transformation of Pt during He treatment, we utilize dynamic nuclear polarization (DNP)-enhanced solid-state nuclear magnetic resonance (SSNMR) spectroscopy and investigate the evolution of Pt site and its circumference. Results obtained from different techniques suggest that He treatment changes the coordination structure of Pt and the elongate of Pt–N bond, which results in the Pt activation and enables the CO coordination. On the contrary, H<sub>2</sub> treatment partially reduces single site Pt ions to form metallic Pt nanoparticles.

## **EXPERIMENTAL**

#### **Sample Preparation**

*Synthesis of MOF-253.* We chose MOF-253 as the support to immobilize Pt atoms due to the availability of uncoordinated bipyridine functional groups on MOF linkers for metal coordination, besides its high thermal stability up to 350 °C. The Al-MOF is synthesized according to reported literature with slight modifications.<sup>31</sup> In a 20-mL scintillation vial, 2,2'-bipyridine-5,5'-dicarboxylic acid (244.5 mg, 1.0 mmol) is dissolved 20 mL dimethylformamide (DMF). Aluminum chloride hexahydrate (241 mg, 1.0 mmol) is added to the DMF solution and sonicated for 5 minutes. The solution is capped and transferred to a pre-heated 120 °C oven and incubated for 24 h. After cooling to room temperature, the precipitate is isolated by centrifugation at 7500 rcf for 5 minutes. The isolated solid is washed with a copious amount of DMF, followed by the solvent exchange with acetone, and then dried at 80 °C in oven.

Synthesis of Pt@MOF. MOF-253 (100 mg, 0.175 mmol) and  $Pt(DMSO)_2Cl_2$  (38.6 mg, 16 wt% Pt, 91.0  $\mu$ mol) are dispersed in 10 mL of acetonitrile in a 6-dram vial. The suspension is heated to 80 °C under stirring for 12 h in an oil bath. The yellow solid is isolated by centrifugation at 4000 rcf for 5

minutes. The isolated solid is washed with 10 mL hot acetonitrile at 60 °C three times by centrifugation. The solid is dried in the oven at 80 °C. ICP-MS analysis of the yellow solid upon Pt insertion shows that the metal loading for Pt is 13 wt%. The obtained sample is denoted as Pt@MOF.

*Post-synthesis treatment of Pt@MOF*. Since Pt@MOF is inactive for CO adsorption (see Fig. S1 in Supplemental Material), the as-synthesized sample is activated under a dynamic 10% H<sub>2</sub>/Ar flow for 2 h or a He flow for 2~16 h at 300 °C. The treated samples are exposed to a CO flow (10 ml/min) for 20 min. The samples are referred to as Pt@MOF-XY/Z, where X is the duration of pretreatment, Y is the type of gas used for the pretreatment, and Z is the presence or absence of CO adsorption. For example, Pt@MOF-16He/CO denotes the sample treated with He for 16 h, followed by CO adsorption.

#### Materials characterization

*Powder X-ray diffraction (PXRD)*. The PXRD patterns are recorded at room temperature using a Bruker D8 Advance diffractometer with Ni-filtered Cu Kα radiation (1.5418 Å) at 40 kV and 40 mA. Inductively coupled plasma mass spectrometry (ICP-MS) measurements are carried out using a Thermo Fisher Scientific X Series 2 spectrometer. High-resolution AC-STEM imaging is performed on a Titan Themis 300 probed corrected TEM with a Super-X EDX detector.

*X-Ray Photoelectron Spectroscopy (XPS)*. The XPS measurements are performed using a Kratos Amicus/ESCA 3400 instrument. The samples are irradiated with 240 W unmonochromated Mg K $\alpha$  x-rays. The binding energies of all peaks are calibrated using the C1s peak at 284.6 eV as the reference. To prevent the oxidation of metallic Pt in air, Pt@MOF-2H<sub>2</sub> are freshly reduced and protected in Ar atmosphere before the XPS measurement.

*Thermogravimetric analysis and mass spectrometry (TGA-MS)*. TGA-MS is performed on Netzsch DSC/TGA–MS in He flow (40 ml/min). Around 15 mg sample is packed in an alumina crucible and heated with a ramping rate of 20 °C/min to reach 300 °C. The temperature is kept at 300 °C for 5 h. The TGA mass-loss is recorded after background correction to empty alumina crucible.

*Brunauer-Emmett-Teller (BET) surface area*. BET surface area measurement of the catalysts is performed by nitrogen sorption isotherms at 77 K using Micromeritics 3Flex surface characterization analyzer. Approximately 50 mg Pt@MOF samples are degassed under vacuum (~5 x 10<sup>-5</sup> torr) at specific conditions before the measurement (100 °C for 6 h or 300 °C for 16 h).

*Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS).* The DRIFTS measurements are performed using an Agilent Cary 670 FTIR equipped with a linearized Mercury-Cadmium-Telluride (MCT) detector, a Harrick diffuse reflectance accessory, and a Praying Mantis high-temperature reaction chamber. All spectra are recorded at a resolution of 2 cm<sup>-1</sup> from 700 – 4000 cm<sup>-1</sup> under atmospheric pressure.

About 20 mg of the sample powder is packed into the IR sample holder equipped with KBr windows. KBr is used as the background, and the background is taken at 30 °C under He. The sample is activated under dynamic He flow at 300 °C for 16 h. In-situ IR spectra are collected continuously during the activation process to study the sample change.

CO adsorption studies are performed using *in situ* DRIFTS. The samples are first activated/reduced at the designated condition (*vide supra*). After cooling to 30 °C, a spectrum of the sample is recorded as the background under He atmosphere. Carbon monoxide (10 ml/min) was then introduced for 15 minutes to saturate the accessible Pt surface. The excess gas-phase carbon monoxide is purged from the cell under a dynamic He flows (40 ml/min) for 30 minutes. In-situ IR spectra are collected continuously at variable temperatures under the constant He flow to probe the stability of chemisorbed species.

Dynamic nuclear polarization-enhanced solid-state NMR (DNP-enhanced SSNMR). DNPenhanced <sup>195</sup>Pt{<sup>1</sup>H} BRAIN-CP/WURST-CPMG,<sup>32</sup> <sup>13</sup>C{<sup>1</sup>H}, and <sup>15</sup>N{<sup>1</sup>H} cross-polarization magicangle spinning (CPMAS) is carried out using a Bruker DNP NMR spectrometer operated at 9.4 T, equipped with a gyrotron generating a continuous wave at 263 GHz and a low-temperature magicangle spinning (MAS) probe. The samples are exposed to a 16 mM TEKPol<sup>33</sup> solution of 1,1,2,2tetrachloroethane (TCE) by incipient wetness impregnation in a mortar and then packed into 3.2 mm sapphire MAS rotors. The <sup>195</sup>Pt spectra are recorded under a static condition using 10 ms WURST pulse sweeping over 250 kHz following an initial 2.5  $\mu$ s of <sup>1</sup>H pulse. The spectra consist of 8~10 subspectra, obtained by stepping the carrier frequency in 90 kHz increments.<sup>34</sup>For each sub-spectra, 32 CPMG echoes are accumulated. The <sup>13</sup>C, <sup>15</sup>N, and <sup>195</sup>Pt chemical shifts are reported using the delta scale and are referenced externally to TMS, CH<sub>3</sub>NO<sub>2</sub>, and PtCl<sub>6</sub> in aqueous solution at 0 ppm, respectively.

#### **RESULTS AND DISCUSSION**

Prior to the DRIFTS experiments, the crystallinity of samples is examined by PXRD (Fig. 1a). The diffraction pattern of Pt@MOF shows Braggs peaks at  $2\theta = 6^{\circ}$  and  $12^{\circ}$ , assigned to MOF-253. Compared with MOF-253, the PXRD pattern of Pt@MOF has a low signal-to-noise ratio and broad peaks, indicating the decreased crystallinity of the MOF-253 during Pt loading. The thermal treatments of the Pt@MOF at 300 °C (Pt@MOF-2H<sub>2</sub> and Pt@MOF-16He) cause a small shift of the peak at  $2\theta = 6.4^{\circ}$ , attributing to the thermally induced disorder of the crystal structure.<sup>35</sup> Previously reported TGA study of MOF-253 observed no evident mass loss up to 350 °C.<sup>31</sup> The remained diffraction peaks of MOF after the harsh treatment confirms the good thermal stability of MOF-253. The H<sub>2</sub> reduction yielded Pt nanoparticles, evidenced by the Pt(111) and Pt(200) peak at  $2\theta = 40$  and  $47^{\circ}$ , respectively. Indeed, Pt nanoparticles are found in the AC-STEM images of Pt@MOF-2H<sub>2</sub> (Fig 1c, d) in addition to single Pt atoms, and the particle size is measured to be ~4 nm (Fig. 1b). In contrast, the formation of Pt nanoparticles is not detected in Pt@MOF-16He, despite the longer treatment time at 300 °C.



**Fig. 1.** (a) PXRD patterns of MOF-253, Pt@MOF, Pt@MOF-2H<sub>2</sub>, and Pt@MOF-16He. (b) The size distribution of Pt nanoparticles in Pt@MOF-2H<sub>2</sub> (100 counts). AC-STEM images of (c, d) Pt@MOF-2H<sub>2</sub> and (e, f) Pt@MOF-16He. The red arrows indicate the isolated single Pt atoms.

The oxidation state of Pt in Pt@MOF-2H<sub>2</sub> is evaluated by XPS. The Pt 4f7/2 peak in Pt@MOF is located at 72.5 eV that can be assigned to cationic Pt(II) (Fig. 2a). Upon coordination of PtCl<sub>2</sub>(DMSO)<sub>2</sub> to the bipyridine linker of MOF-253, the Pt remains cationic as suggested in a previous study.<sup>36</sup> After thermal treatment under H<sub>2</sub> for 2 h, approximately 12% of Pt is indeed reduced to metallic Pt(0) (Fig. 2b). Note the additional deconvoluted peak at 74.5 eV is a contribution from the Al 2p of the secondary building unit in MOF-253.<sup>37</sup>



**Fig. 2.** Pt 4f XPS spectra of (a) Pt@MOF and (b) Pt@MOF-2H<sub>2</sub>. Red line: Pt<sup>2+</sup> 4f<sub>5/2</sub> and Pt<sup>2+</sup> 4f<sub>7/2</sub>. Green line: Pt<sup>0</sup> 4f<sub>5/2</sub> and Pt<sup>0</sup> 4f<sub>7/2</sub>. Blue line: Al 2p of the secondary building unit in MOF-253.

Measuring vibration bands of adsorbed CO by DRIFTS (CO-DRIFTS) is a broadly used technique to characterize Pt isolated sites and continuous surface in catalysts. We find that CO could not adsorb on as-synthesized Pt@MOF without any thermal treatment (Fig. S1). Fig. 3a shows the CO-DRIFTS spectra from Pt@MOF-xHe/CO (thermal treatment in hours, x = 2, 4, 8, and 16), where a major CO

adsorption band at 2109 cm<sup>-1</sup> appears along with a shoulder peak at 2094 cm<sup>-1</sup>. The intensities of the two peaks increase with the thermal treatment time under He, indicating more active Pt sites are generated for CO adsorption. Empirically, peaks above 2100 cm<sup>-1</sup> are assigned to CO adsorption on cationic Pt.38 We speculate the peak at 2094 cm-1 could be ascribed to CO adsorbed on the Pt coordinating to nitrogen of different electronic properties due to the existence of defects in MOF-253, which needs to be further explored. For the sample reduced under H<sub>2</sub> for different amounts of time, we observe an additional CO adsorption peak at 2061 cm<sup>-1</sup> that could be assigned to the linearly adsorbed CO on metallic Pt surface (Fig. S1), which is consistent with the results from PXRD and AC-STEM. The increased intensity of the 2061 cm<sup>-1</sup> peak with the extended thermal treatment time under H<sub>2</sub> indicates the formation of more metallic Pt surface upon more prolonged reduction. For thermal treatment under the non-reducing He environment, the absence of 2061 cm<sup>-1</sup> peak for Pt@MOF-xHe/CO suggests that the isolated Pt sites are stable and do not agglomerate to nanoparticles.<sup>39</sup> The Pt sites are indeed activated by the He treatment for CO adsorption, and their integrated intensities increase 26-fold by extending the treatment time from 2 to 16 h. In contrast, the appearance of peak at 2061 cm<sup>-1</sup> in Pt@MOF under different reducing conditions (Fig. S1) demonstrates that the isolated Pt site is not stable upon reduction at 300 °C.



**Fig. 3.** (a) DRIFTS spectra of CO adsorbed on Pt@MOF with different He activation times at 300 °C. (b) Integrated peak areas of CO adsorption DRIFTS spectra measured from Pt@MOF samples with different He activation times.

To further explore the activation process, in-situ DRIFTS spectra are recorded for Pt@MOF during the thermal treatment under He flow. With increasing sample temperature, the broad water peak gradually decreases and finally disappears at 300 °C (shaded area in Fig. 4a). Along with the water peak, we also notice the intensity changes of peaks centered at 2931, 2252, 2292 cm<sup>-1</sup>, which are assigned to v(C–H),  $\nu$  (C=N), and combination bands of  $\delta$ (C–H) and v(C–C).<sup>40-42</sup> These observations suggest that water and acetonitrile (the solvent used for loading Pt) remain in Pt@MOF after drying at 80 °C, which can be removed upon further thermal treatment under He. TGA-MS experiment reveals that these species are readily removed upon heating (Fig. 4b). Both DRIFTS and TGA-MS results show that water and acetonitrile are removed below 300 °C. Extending the thermal treatment at 300 °C to 16 h under He does not induce further changes in DRIFTS spectra but a slight decrease in the sample weight from TGA (< 2%). Considering the dramatically increased CO adsorption with the thermal treatment time at 300 °C under He (Fig. 3), the results in Fig. 4 suggests that site-blocking by the remaining solvent or water molecules is unlikely to be the reason for the inactive nature of assynthesized Pt@MOF for CO adsorption. We also confirm that CO molecules do not adsorb on Pt@MOF after 2 h thermal treatment at 200 °C under He.



**Fig. 4.** (a) DRIFTS spectra of Pt@MOF measured at different temperatures and He activation time at 300 °C. (b) TGA-MS result of as-synthesized Pt@MOF. Inset: MS signal of acetonitrile during TGA (m/z=41).

We further explore the stability of the adsorbed CO in Pt@MOF-16He/CO by measuring DRIFTS spectra of the temperature-dependent desorption of CO under He flow (Fig. 5). Both peaks at 2109 and 2094 cm<sup>-1</sup> decrease gradually but are still visible even at 300 °C. Note that the peak positions of these two vibrational bands shift toward lower frequency (red-shift) by 5 cm<sup>-1</sup> and 8 cm<sup>-1</sup>, respectively. These two peaks do not fully reverse to their initial position after the sample cools down to room temperature, suggesting permanent structural changes in the Pt@MOF. We raise the catalyst temperature to 300 °C again and keep it for an additional 6 h. The peaks do not disappear after 6 h, indicating strong CO coordination to the isolated Pt sites. We also do not observe any new CO

adsorption peaks appear at 2061 cm<sup>-1</sup> during the whole thermal treatment process, indicating the high thermal stability of isolated Pt sites (Fig. S2). We also test the stability of adsorbed CO on Pt@MOF-2H<sub>2</sub> (Fig. S3). The intensities of the two vibrational bands at 2109 and 2061 cm<sup>-1</sup> decrease gradually with the increase of temperature. The peak intensity at 2061 cm<sup>-1</sup> decreases relatively faster than the peak at 2109 cm<sup>-1</sup> due to the stronger coordination of CO with cationic Pt sites than that on metallic Pt surface.<sup>30</sup> Unlike Pt@MOF-16He, both of these two peaks disappear before the thermal treatment temperature reaches 300 °C.



**Fig. 5.** Time-dependent DRIFTS spectra of adsorbed CO on Pt@MOF with 16 h He treatment from 30 °C to 300 °C under He flow.

To further scrutinize the Pt site and its circumference, the samples are characterized by using DNPenhanced SSNMR spectroscopy. The <sup>195</sup>Pt spectrum of Pt@MOF identifies the Pt site as cis-Pt(bipy)Cl<sub>2</sub>,<sup>36</sup> and changes significantly after the He/CO treatments (Fig. 6). In contrast, the <sup>13</sup>C{<sup>1</sup>H} CPMAS spectra (Fig. 6b) show only minor changes upon the He/CO treatment; i) a weak acetonitrile signal ( $\delta_{13C} = 2$  ppm) found in the spectrum of Pt@MOF disappears, and ii) a signal from carboxyl carbon in the linker ( $\delta_{13C} = 171$  ppm) is broadened. Most likely, the lack of signal from adsorbed CO is owing to the absence of protons in close proximity to the CO. The <sup>15</sup>N{<sup>1</sup>H} CPMAS spectrum of Pt@MOF shows three signals at  $\delta_{15N} = -74$ , -141, and -175 ppm, assigned to the bipyridine, acetonitrile, and bipyridine coordinated to Pt (Fig. 6c).<sup>36,43,44</sup> When nitrogen coordinates to metals, its resonance frequency shifts toward higher field, so-called metal coordinating shift.<sup>45</sup> Indeed, the resonance frequency of the pyridine nitrogen shift from -74 ppm to -175 ppm upon coordinating to Pt(II). A shoulder peak at around -85 ppm is attributed most likely to the structural inhomogeneity of the MOF-253 because the shoulder peak is also observed in the as-synthesized MOF-253 (see Fig. S4). The absence of the metal coordinating shift in the acetonitrile signal indicates that the acetonitrile is not coordinating to the Pt site, which is consistent with the structure of Pt site identified by the <sup>195</sup>Pt NMR. <sup>36</sup> After the He/CO treatment, the -141 ppm <sup>15</sup>N signal disappears and the intensity of -175 ppm signal decreases, while a new signal appears at -133 ppm. The disappearance of both  $\delta_{13C} = 2$  ppm and  $\delta_{15N} = -141$  ppm signals indicates the removal of acetonitrile. The decrease of  $\delta_{15N} = -175$  ppm signal and the appearance of  $\delta_{15N} = -133$  ppm signal are likely attributed to the structural transformation of Pt site. This deshielding shift suggests elongation of Pt–N distance that weakens the Pt–N interactions and consequently enables CO insertion. The broadening of  $\delta_{13C} = 171$  ppm signal also implies the structural change of the frameworks and/or the cornerstones. Note that all changes shown in the <sup>13</sup>C and the <sup>15</sup>N spectra are also found in those of Pt@MOF-16He (Fig. S5), which suggests that the observed changes are caused by the He treatment.

The above-mentioned evolutions of the Pt sites are substantiated further by the quantitative analysis of <sup>15</sup>N spectra. Although the CPMAS experiment is not a truly quantitative technique, the signal intensities from spins in a similar environment provide reasonable approximations in a relative manner (Table 1). In both Pt@MOF-2He/CO and Pt@MOF-16He/CO, the intensities of -133 ppm <sup>15</sup>N peak are similar to the decrease of -175 ppm signal upon the He/CO treatment, and consequently the ratio of <sup>15</sup>N peaks from uncoordinated ( $\delta_{15N} \sim -74$  ppm) and coordinated ( $\delta_{15N} \sim -133$  ppm and -175 ppm) signals is constant. Most likely, the change of whole <sup>195</sup>Pt NMR spectrum suggests the elongation of one of Pt-N bonds in the majority Pt sites, rather than the elongation of both Pt-N bonds in a part of Pt sites.



**Fig. 6.** DNP-enhanced (a) <sup>195</sup>Pt{<sup>1</sup>H} BRAIN-CP/WURST-CPMG, (b) <sup>13</sup>C{<sup>1</sup>H} CPMAS, and (c) <sup>15</sup>N{<sup>1</sup>H} CPMAS spectra of Pt@MOF (top), Pt@MOF-2He/CO (middle), and Pt@MOF-16He/CO (bottom).

**Table 1.** 15N Signal Intensity of samples.

Samples	-75 ppm <sup>a</sup>	-133 ppm	-175 ppm	coordinated nitrogen (%)
Pt@MOF	0.73	0	0.27	0.27
Pt@MOF-2He/CO	0.74	0.05 (+0.05) <sup>b</sup>	0.21 (-0.06) <sup>b</sup>	0.26
Pt@MOF-16He/CO	0.73	0.14 (+0.14) <sup>b</sup>	0.13 (-0.14) <sup>b</sup>	0.27

a) The spinning sidebands (not seen in the spectra) are also accounted. b) The numbers in parentheses represent the decrease of signal intensity from that of Pt@MOF.

Based on the findings from SSNMR as well as XRD, XPS, TGA-MS, and DRIFTS, the evolution of coordination structures shown in Scheme 1 is suggested. The partial degradation/deformation of the framework of Pt@MOF could be caused by thermal treatment under He, indicated by the decreased PXRD peak intensity (Fig. 1a) and BET surface area (Fig. S6). The thermal treatment under He induces elongation of one of the Pt-N bonds in as-synthesized Pt@MOF (Scheme 1b). Most likely, this distorted coordination structure of the Pt site enables the additional adsorption of CO (Scheme 1c). Indeed, such 5-coordinated Pt(II) complexes are reported in earlier studies.<sup>46-48</sup>



Scheme 1. Potential evolutions of the coordination structure of Pt(II) centers in MOF-253.

#### CONCLUSIONS

In summary, we used the surface sensitive DRIFTS with CO as the probe molecule to study the stability and structural transformation of the isolated single Pt sites during thermal treatments under reductive or inert conditions. We found the prerequisite of high-temperature He treatment for the activation of Pt sites for CO adsorption. Thermal treatment under He does not cause Pt reduction and aggregation, in contrast to that under H<sub>2</sub>. Using DNP-enhanced SSNMR spectroscopy, we identified the high-temperature activation in He leads to change of local coordination of the isolated Pt sites by elongating and weakening the Pt–N bond, which enables CO adsorption to form 5-coordinated Pt(II) complex. We envision that the deep understanding of structure evolution of Pt could shed light on the rational design of SACs and the evaluation of their catalytic performance.

## ASSOCIATED CONTENT

**Supplementary Materials**. The supplementary material includes DRIFTS spectra of CO adsorption on Pt@MOF with different treatments, DNP-enhanced 13C{<sup>1</sup>H} CPMAS, and 15N{<sup>1</sup>H} CPMAS spectra of Pt@MOF-16He and N<sub>2</sub> adsorption/desorption isotherms of Pt@MOF.

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#### Notes

The authors declare no competing financial interest.

## **Data Availability Statements**

The data that supports the findings of this study are available within the article and its supplementary material.

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## References

1. H. Yamashita, K. Mori, Y. Kuwahara, T. Kamegawa, M. Wen, P. Verma, M. Che, Chem. Soc. Rev. 47, 8072 (2018).

2. K. M. Choi, D. Kim, B. Rungtaweevoranit, C. A. Trickett, J. T. D. Barmanbek, A. S. Alshammari, P. Yang, O. M. Yaghi, J. Am. Chem. Soc. **139**, 356 (2017).

3. T. Zhou, Y. Du, A. Borgna, J. Hong, Y. Wang, J. Han, W. Zhang, R. Xu, Energy Environ. Sci. 6, 3229 (2013).

- 4. X. Yang, J.-K. Sun, M. Kitta, H. Pang, Q. Xu, Nat. Catal. 1, 214 (2018).
- 5. T. He, P. Pachfule, H. Wu, Q. Xu, P. Chen, Nat. Rev. Mater. 1, 16059 (2016).
- 6. C. Wang, K. E. deKrafft, W. Lin, J. Am. Chem. Soc. 134, 7211 (2012).
- 7. C. Rivera-Cárcamo, P. Serp, ChemCatChem 10, 5058 (2018).
- 8. A. Wang, J. Li, T. Zhang, Nat. Rev. Chem. 2, 65 (2018).
- 9. Z. Liang, C. Qu, D. Xia, R. Zou, Q. Xu, Angew. Chem. Int. Ed. 57, 9604 (2018).

10. S. M. J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A. I. Olivos-Suarez, A. Sepúlveda-Escribano, A. Vimont, G. Clet, P. Bazin, F. Kapteijn, M. Daturi, E. V. Ramos-Fernandez, F. X. Llabrés i Xamena, V. Van Speybroeck, J. Gascon, Chem. Soc. Rev. **46**, 3134 (2017).

- 11. T. Drake, P. Ji, W. Lin, Acc. Chem. Res. **51**, 2129 (2018).
- 12. H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, Science 341, (2013).
- 13. O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, Nature 423, 705 (2003).
- 14. J. Gascon, A. Corma, F. Kapteijn, F. X. Llabrés i Xamena, ACS Catal. 4, 361 (2013).
- 15. A. Corma, H. García, F. X. Llabrés i Xamena, Chem. Rev. 110, 4606 (2010).
- 16. C. Wang, Z. Xie, K. E. deKrafft, W. Lin, J. Am. Chem. Soc. 133, 13445 (2011).
- 17. K. Manna, T. Zhang, M. Carboni, C. W. Abney, W. Lin, J. Am. Chem. Soc. 136, 13182 (2014).
- 18. K. Manna, T. Zhang, W. Lin, J. Am. Chem. Soc. 136, 6566 (2014).
- 19. K. Manna, T. Zhang, F. X. Greene, W. Lin, J. Am. Chem. Soc. 137, 2665 (2015).
- 20. L. Cao, Z. Lin, F. Peng, W. Wang, R. Huang, C. Wang, J. Yan, J. Liang, Z. Zhang, T. Zhang, L. Long, J. Sun, W. Lin, Angew. Chem. Int. Ed. **55**, 4962 (2016).

21. S. Øien, G. Agostini, S. Svelle, E. Borfecchia, K. A. Lomachenko, L. Mino, E. Gallo, S. Bordiga, U. Olsbye, K. P. Lillerud, C. Lamberti, Chem. Mater. **27**, 1042 (2015).

22. X. Fang, Q. Shang, Y. Wang, L. Jiao, T. Yao, Y. Li, Q. Zhang, Y. Luo, H.-L. Jiang, Adv. Mater. **30**, 1705112 (2018).

23. C. Copéret, W.-C. Liao, C. P. Gordon, T.-C. Ong, J. Am. Chem. Soc. 139, 10588 (2017).

24. L. DeRita, S. Dai, K. Lopez-Zepeda, N. Pham, G. W. Graham, X. Pan, P. Christopher, J. Am. Chem. Soc. **139**, 14150 (2017).

25. K. Ding, A. Gulec, A. M. Johnson, N. M. Schweitzer, G. D. Stucky, L. D. Marks, P. C. Stair, Science **350**, 189 (2015).

26. L. Cao, Q. Luo, W. Liu, Y. Lin, X. Liu, Y. Cao, W. Zhang, Y. Wu, J. Yang, T. Yao, S. Wei, Nat. Catal. **2**, 134 (2019).

- 27. Y. Chen, S. Ji, C. Chen, Q. Peng, D. Wang, Y. Li, Joule 2, 1242 (2018).
- 28. W. Qu, X. Liu, J. Chen, Y. Dong, X. Tang, Y. Chen, Nat. Commun. 11, 1532 (2020).
- 29. J. Liu, Chin. J. Catal. **38**, 1460 (2017).
- 30. K. Ding, A. Gulec, A. M. Johnson, N. M. Schweitzer, G. D. Stucky, L. D. Marks, P. C. Stair, Science **350**, 189 (2015).
- 31. E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long, O. M. Yaghi, J. Am. Chem. Soc. **132**, 14382 (2010).

32. K. J. Harris, A. Lupulescu, B. E. G. Lucier, L. Frydman, R. W. Schurko, J. Magn. Reson. 224, 38 (2012).

33. A. Zagdoun, G. Casano, O. Ouari, M. Schwarzwälder, A. J. Rossini, F. Aussenac, M. Yulikov, G. Jeschke, C. Copéret, A. Lesage, P. Tordo, L. Emsley, J. Am. Chem. Soc. **135**, 12790 (2013).

34. D. Massiot, I. Farnan, N. Gautier, D. Trumeau, A. Trokiner, J. P. Coutures, Solid State Nucl. Magn. Reson. **4**, 241 (1995).

35. F. Carson, S. Agrawal, M. Gustafsson, A. Bartoszewicz, F. Moraga, X. Zou, B. Martin-Matute, Chem. Eur. J. **18**, 15337 (2012).

36. T. Kobayashi, F. A. Perras, T. W. Goh, T. L. Metz, W. Huang, M. Pruski, J. Phys. Chem. Lett. 7, 2322 (2016).

- 37. C. M. Moran, J. N. Joshi, R. M. Marti, S. E. Hayes, K. S. Walton, J. Am. Chem. Soc. 140, 9148 (2018).
- 38. Q. Xu, Coord. Chem. Rev. **231**, 83 (2002).

39. C. L. Whitford, C. J. Stephenson, D. A. Gómez-Gualdrón, J. T. Hupp, O. K. Farha, R. Q. Snurr, P. C. Stair, J. Phys. Chem. C **121**, 25079 (2017).

40. G. Busca, T. Montanari, M. Bevilacqua, E. Finocchio, Colloids Surf, A Physicochem Eng Asp **320**, 205 (2008).

41. I. Ortiz-Hernandez, D. J. Owens, M. R. Strunk, C. T. Williams, Langmuir 22, 2629 (2006).

42. N. S. Marinković, M. Hecht, J. S. Loring, W. R. Fawcett, Electrochim. Acta 41, 641 (1996).

43. R. L. Gdula, M. J. A. Johnson, N. W. Ockwig, Inorg. Chem. 44, 9140 (2005).

44. L. Pazderski, E. Szlyk, J. Sitkowski, B. Kamienski, L. Kozerski, J. Tousek, R. Marek, Magn. Reson. Chem. 44, 163 (2006).

45. L. Pazderski, Chapter Two - 15N and 31P NMR Coordination Shifts in Transition Metal Complexes with Nitrogen- and Phosphorus-Containing Heterocycles. In Annual Reports on NMR Spectroscopy, Webb, G. A., Ed. Academic Press: 2013; Vol. 80, pp 33.

46. L. Maresca, G. Natile, Comments Inorg. Chem. 14, 349 (1993).

47. F. P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. Tiripicchio, G. Pacchioni, J. Chem. Soc. Chem. Comm. 333 (1992).

48. A. Annunziata, M. E. Cucciolito, R. Esposito, G. Ferraro, D. M. Monti, A. Merlino, F. Ruffo, Eur. J. Inorg. Chem. **2020**, 918 (2020).