

RESEARCH ARTICLE

Quantifying Microenvironment Effect on Metal Electronic Structure With Experimentally Accessible Descriptor: Examples of MOF-Incorporated Pt Catalysts

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ABSTRACT

The chemical microenvironment surrounding metal nanoparticles (NPs) plays crucial roles in regulating their electronic structures. However, due to the lack of quantitative descriptor, such effect has been understood largely in a qualitative manner. To address this issue, a series of reticular metal-organic frameworks (MOFs) with diverse functional groups (MIP-206-X, X = OH, OCH₃, H, Cl, and F) were synthesized, and Pt NPs with similar sizes and loadings were incorporated to afford Pt@MIP-206-X for ammonia borane methanolysis. X-ray absorption near edge structure (XANES) was adopted to determine the d-orbital occupancy of Pt, and the electronic contribution from MOFs was quantified as the descriptor Δe , which was demonstrated to accurately describe the Pt-methanol adsorption strength (quantified by activation entropy and methanol desorption temperature) and exhibit an excellent linear correlation with catalytic activity. Isotopic analyses and DFT calculations revealed that a larger Δe strengthens methanol adsorption on Pt, promotes O–H bond cleavage as the rate-determining step (RDS), and leads to enhanced activity.

1 | Introduction

For supported metal catalysts, the electronic structure of metal centers is of great importance in determining their catalytic performance [1–6]. According to the d-band center theory [7, 8], it governs substrate interactions, thereby determining catalytic activity. As seen in enzymes, electronic state of metal center is strongly influenced by the surrounding chemical microenvironment; consequently, extensive efforts have been devoted to modulating this microenvironment to optimize performance [9–16]. These elegant reports establish qualitative corre-

lations between the chemical microenvironment, the electronic state of metal centers and their catalytic activity. Despite the progress, a precise quantitative relationship among them, though highly desired and essential to guide the design and synthesis of heterogeneous catalysts [17–19], has not yet been clearly established.

To achieve this goal, recent studies explored the quantitative relationship between electronic structure and catalytic performance through methods such as alloying and metal-support interactions, with successful applications in some

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systems [20–27]. Notwithstanding these valuable efforts, the models adopted in these studies to modulate electronic state of metal sites more or less introduce additional variables, such as size [21, 23], morphology [25], composition [22, 26], and bond length [27] of metal NPs, which may also influence catalytic performance. These variables not only interfere with the quantitative correlation between metal electronic structure and catalytic activity but also make it difficult to independently investigate the effect of the chemical microenvironment on the metal's electronic structure. On the other hand, the electronic structure regulation of metal NPs is generally uneven in traditional supported metal catalysts—stronger at the metal-support interface and weaker at noninterface regions [20, 28, 29]. Overall, the parameters affecting the resulting performance in a catalytic system are complex; it is challenging to control all parameters while regulating electronic structure of metal centers as the sole variable. To this end, it is necessary to develop suitable supports that can create uniform chemical microenvironment around metal centers, while regulating electron transfer between the support and metal center without introducing additional variables.

Metal-organic frameworks (MOFs) [30–34], a class of crystalline porous materials with well-defined structures, high porosity, and tunable pore wall environments, have been intensively demonstrated to be promising supports for metal NPs toward catalytic applications [35–39]. The customizable pore structures of MOFs can effectively incorporate metal NPs without disturbing substrate accessibility [40–45]. More importantly, the functional groups on the MOF pore walls can be flexibly tailored, thereby creating modulated microenvironment to enable tailored electronic properties for encapsulated metal NPs, without altering other parameters. This makes MOFs an ideal platform for investigating the quantitative relationship among modulated microenvironment, metal electronic structure, and catalytic performance. However, to date, the electron transfer between chemical microenvironment and metal center remains unquantified, and finding a suitable descriptor to quantify this property is highly desired yet very challenging to describe the quantitative relationship among the three.

In this work, a series of isorecticular MOFs with different functional groups, named MIP-206-X (X = OH, OCH₃, H, Cl, and F), have been synthesized, followed by incorporating Pt NPs to afford Pt@MIP-206-X for the methanolysis of ammonia borane (Scheme 1). Significantly, the resulting Pt@MIP-206-X exhibit distinctly different activities, despite similar Pt sizes and loadings. By fixing possible interfering parameters, the d-orbital occupancy of Pt is evaluated by x-ray absorption near edge structure (XANES), and the electronic contribution from MOFs to Pt is quantified, affording the descriptor Δe , which has been confirmed as an excellent descriptor for both Pt-methanol adsorption strength and catalytic activity (Scheme 1, right). Mechanistic studies reveal that a larger Δe leads to stronger Pt adsorption of methanol (described by the activation entropy, ΔS^{0*}), facilitating the O-H activation of methanol and thereby enhancing the catalytic activity (described by turnover frequency, simply as TOF).

TABLE 1 | The Pt content, size, and corresponding Pt dispersion (D_{Pt}) evaluated by CO chemisorption over Pt@MIP-206-X composites.

Entries	Groups (-X)	Pt (wt%)	D_{Pt} (%)	Size (nm) ^a	Size (nm) ^b
1	OH	1.58	88.60	1.27	1.5 ± 0.4
2	OCH ₃	1.58	87.07	1.30	1.5 ± 0.4
3	H	1.50	77.74	1.45	1.6 ± 0.4
4	Cl	1.50	82.55	1.37	1.5 ± 0.4
5	F	1.59	86.71	1.30	1.5 ± 0.3

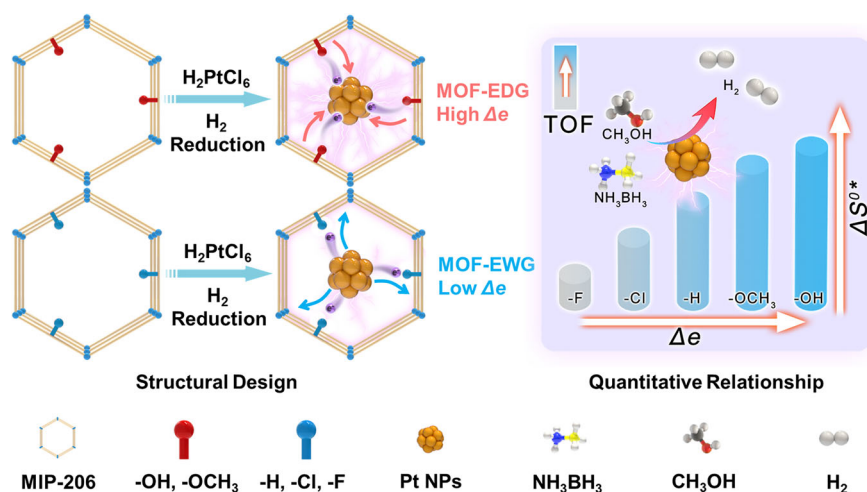
The sizes of Pt NPs are evaluated based on ^aCO chemisorption or ^bHAADF-STEM results.

2 | Results and Discussion

The isorecticular MIP-206-X (X = OH, OCH₃, H, Cl, and F) have been synthesized under solvothermal conditions by reacting zirconium salts with isophthalic acid (IPA) or its functionalized derivatives (5-IPA-X, except for 5-IPA-OCH₃). The MIP-206-OCH₃ was prepared via post-synthetic linker exchange from MIP-206-H [46], with the exchange ratio estimated to be approximately 50%, as determined by nuclear magnetic resonance (NMR) spectroscopy (Figures S1 and S2). Scanning electron microscopy (SEM) images of MIP-206-X reveal similar sizes and morphologies with a small amount of aggregation (Figures 1a and S3). Pt NPs are incorporated into MIP-206-X by introducing H₂PtCl₆ based on a double-solvent approach (DSA) [39], followed by reduction under H₂ atmosphere, to afford Pt@MIP-206-X composites. Powder x-ray diffraction (XRD) patterns show similar high crystallinity and phase purity of MIP-206-X (Figure S4a). Upon introducing Pt NPs, the crystallinity and structural integrity of Pt@MIP-206-X are well preserved (Figure S4b).

Pt NPs are clearly visualized in the HAADF-STEM images (Figure 1b,c), while no apparent Pt NPs appear on the outer surface in the corresponding SE-STEM image (Figure 1d). This contrast strongly suggests that the vast majority of Pt NPs are encapsulated within the MOF particles [47], ensuring uniform microenvironment surrounding Pt NPs. Nitrogen sorption measurements assess the porosity of the Pt@MIP-206-X composites. All samples display similar porous feature (Figure S11), with Brunauer-Emmett-Teller (BET) surface areas ranging from 325 to 595 m²/g. Compared to the pristine MIP-206-X (Figure S12), the slight decrease in BET surface areas further supports successful incorporation of Pt NPs into the MOF pores. To quantify the number of catalytically accessible Pt sites, CO chemisorption titration experiments are conducted on all five composites (Table 1) [48, 49]. The Pt dispersions are evaluated to be 77–89% with particle sizes of 1.27–1.45 nm, which is consistent with the Pt sizes observed in HAADF-STEM images (Figures 1b and S5).

To elucidate the electron transfer between MIP-206-X and Pt NPs, L₃-edge XANES spectra have been recorded. The white line peak is assigned to the electron transition from the 2p_{3/2} orbital to the 5d orbital of Pt, reflecting the density of unoccupied



SCHEME 1 | Schematic illustration showing the synthesis of Pt@MIP-206-X (X = OH, OCH₃, H, Cl, and F) and the corresponding quantitative relationship among Δe , $\Delta S^\ddagger$, and TOF of Pt NPs toward the methanolysis of ammonia borane. EDG and EWG denote electron-donating groups (EDG) and electron-withdrawing groups, respectively.

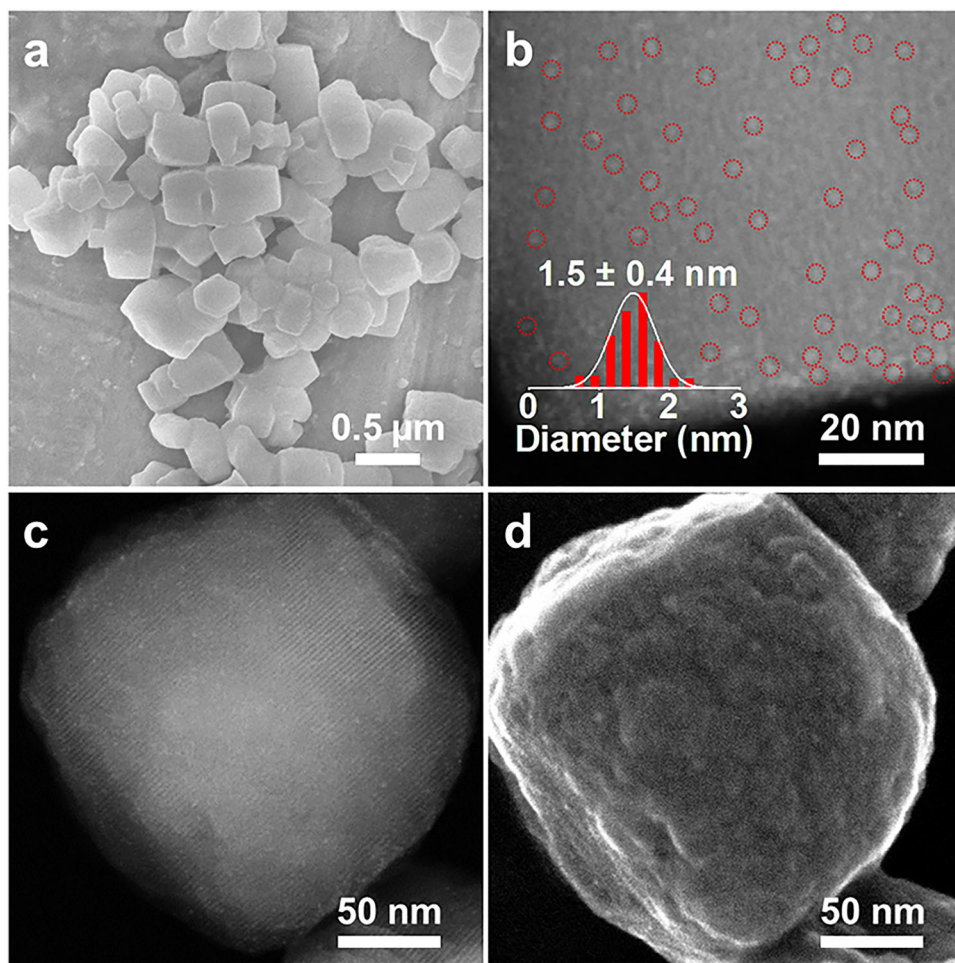


FIGURE 1 | (a) SEM image of MIP-206-OH. (b) HAADF-STEM image of Pt@MIP-206-OH (inset: size distribution of Pt NPs). (c) HAADF-STEM and (d) the corresponding SE-STEM images of Pt@MIP-206-OH.

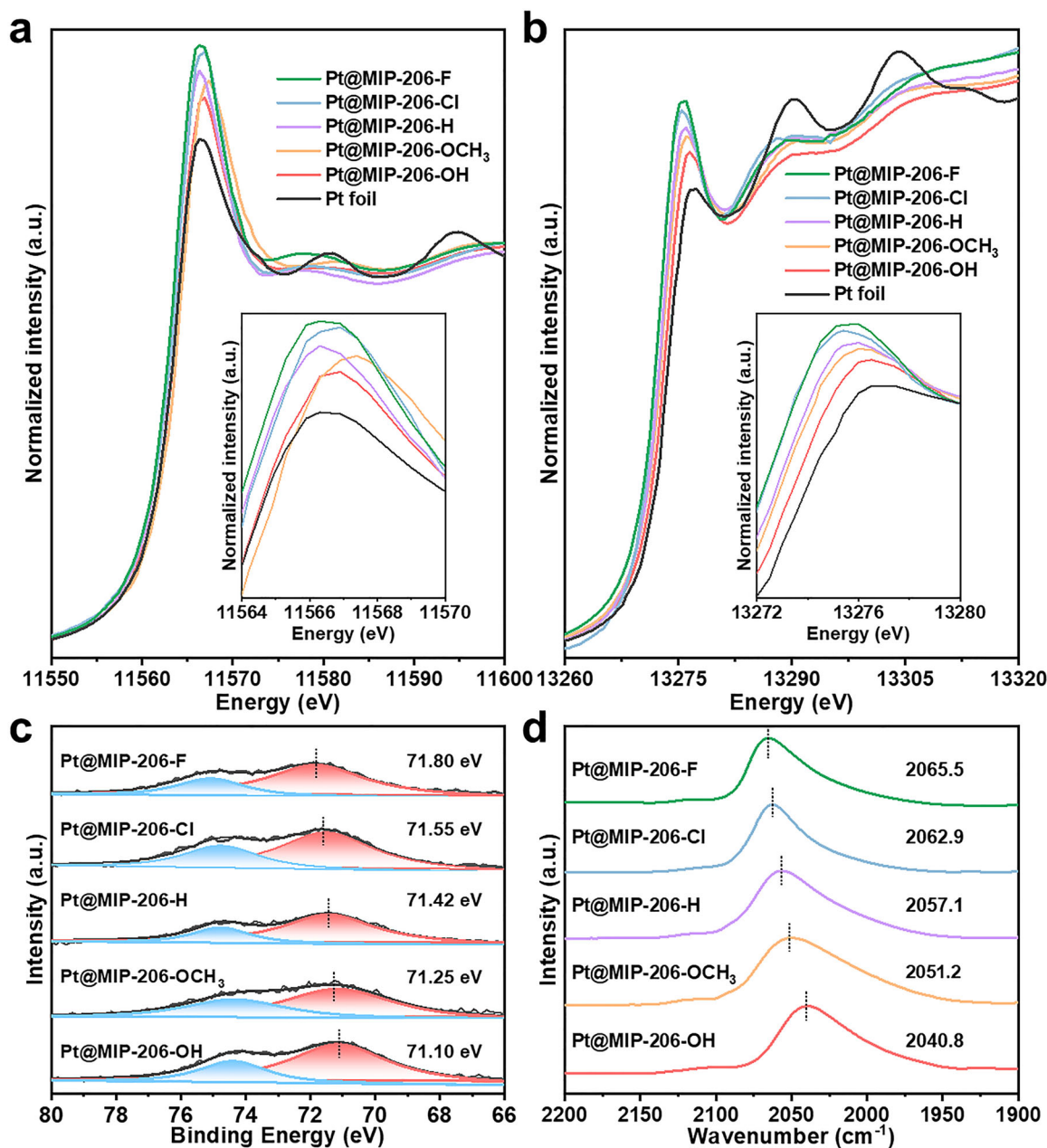


FIGURE 2 | (a) Pt L_3 -edge XANES spectra and (b) Pt L_2 -edge XANES spectra (Insets: enlarged concerned peaks). (c) Pt 4f XPS spectra and (d) CO-DRIFTS spectra of Pt@MIP-206-X (X = OH, OCH₃, H, Cl, and F).

5d states. Increased white line peak is associated with a higher transition probability, indicating greater 5d orbital vacancy [50]. Accordingly, the white line intensity is regarded as an indicator of the d-orbital occupancy of Pt. From the XANES spectra of the five Pt@MIP-206-X composites (Figure 2a), which give overall spectral shapes and white line intensities that are very similar to those of a Pt foil reference and far different from PtO₂ reference (Figure S13), confirming that the Pt species is in the metallic state. Notably, the weakest white line intensity is observed for Pt@MIP-206-OH, indicating the Pt in this catalyst has the most electron filling in its d orbitals.

From the above white line intensity, the Pt d-orbital electron density decreases in the order: Pt@MIP-206-OH > Pt@MIP-206-OCH₃ > Pt@MIP-206-H > Pt@MIP-206-Cl > Pt@MIP-

206-F. This result clearly indicates that charge transfer occurs between the MOFs and the d orbitals of Pt NPs, with Pt on EDG MOFs exhibiting higher d-orbital occupancy than that on electron-withdrawing group (EWG) MOFs. To further quantify the electron transfer between the MOFs and Pt NPs, XANES measurements at the Pt L_2 -edge are conducted (Figure 2b), showing the same trend as the L_3 -edge results, verifying the order of electron-donating ability across different MOFs. The integrated white line peak areas from both L_3 and L_2 edges are adopted to quantify the electron transfer between the MOFs and Pt [51], defined as the descriptor, Δe . Using Pt@MIP-206-H as the reference, the Δe spans from -0.04306 to 0.02539 e (Table S1).

The electronic density of Pt has been investigated by x-ray photoelectron spectroscopy (XPS) (Figure 2c). The Pt 4f binding

energies exhibit a clear trend: Pt@MIP-206-OH < Pt@MIP-206-OCH₃ < Pt@MIP-206-H < Pt@MIP-206-Cl < Pt@MIP-206-F, indicating that Pt incorporated in MIP-206-OH is the most electron-rich, whereas Pt in MIP-206-F is the most electron-deficient. Additionally, CO adsorption diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results give further support (Figure 2d). As an established probe for Pt surface electronic properties, the CO vibrational frequency displays a redshift with increasing surface negative charge [52]. All composites present linear CO adsorption vibrational peaks at 2066–2040 cm⁻¹, with peak positions in the following order: Pt@MIP-206-OH < Pt@MIP-206-OCH₃ < Pt@MIP-206-H < Pt@MIP-206-Cl < Pt@MIP-206-F, demonstrating a gradual decrease in Pt surface electron density. Both XPS and CO-DRIFTS results show that the electron density of Pt NPs follows the electron-donating ability of the MOFs, indicating that the electronic state of Pt can be precisely regulated by the chemical microenvironment created by the MOFs.

Motivated by the above results, catalytic methanolysis of ammonia borane for hydrogen production over Pt@MIP-206-X (X = OH, OCH₃, H, Cl, and F) has been investigated. Given its high hydrogen content (19.6%), ammonia borane has been widely regarded as a promising hydrogen storage material [53]. Moreover, the methanolysis of ammonia borane follows a typical zero-order kinetics with simplified reaction profiles, making it ideal for probing electronic structure-activity relationship of catalysts. All these composites showcase very high activity in this reaction, in which Pt@MIP-206-OH achieves full conversion in 2.61 min, while Pt@MIP-206-OCH₃, Pt@MIP-206-H, Pt@MIP-206-Cl, and Pt@MIP-206-F required 3.25, 4.51, 6.15, and 10.90 min, respectively (Figure 3a). The TOF results can be accurately determined on the basis of the catalytic reaction rates, together with the corresponding Pt loading and dispersion (Table S2), showing a reverse trend with respect to the full conversion time. Powder XRD patterns confirmed preserved crystallinity and structural integrity after the reaction (Figure S14a). HAADF-STEM observation for Pt@MIP-206-OH indicates that Pt NPs remained uniformly dispersed within the MOF particle, with no significant aggregation detected (Figure S14b). A hot filtration experiment over Pt@MIP-206-OH showed that no further conversion of ammonia borane occurred after removal of the catalyst (Figure S15), reflecting the truly heterogeneous nature of the catalytic process. In addition, a linear correlation can be observed between reaction rate and Pt content for Pt@MIP-206-OH with different Pt loadings (Figure S16), indicating that no diffusion or mass transfer limitations are present under the applied conditions [54]. The catalytic activity of Pt@MIP-206-OH remains essentially unchanged in four consecutive reaction cycles, and its crystallinity is well preserved (Figure S17), demonstrating its excellent stability and reusability.

As expected, the activity of these catalysts is positively correlated with their Pt electron density (Figure 2), suggesting that the Pt electronic structure plays a critical role in determining its catalytic behavior. This relationship has been qualitatively explained by various theories and characterizations [9–16], with electronic structure of metal centers considered a key factor in determining their binding strength with substrates. Despite the well-establishment of d-band center theory [7, 8], from an experimental perspective, a quantitative description linking the

binding strength between reactant and metal to the metal's electronic properties, and how this affects catalytic performance, is still lacking yet highly desired. Therefore, an attempt was made to identify the catalytic descriptor by correlating the electronic properties of Pt with its kinetic behavior.

Catalytic experiments at different ammonia borane concentrations were conducted over Pt@MIP-206-OH (Figure S18). The nearly concentration-independent reaction rates indicated that the methanolysis of ammonia borane for hydrogen generation in this system follows zero-order kinetics. Temperature-dependent kinetic studies have been conducted (Figure S19). Reaction rate constants (*k*) are determined for all catalysts at varied temperatures, enabling the evaluation of activation energies (*E_a*) and pre-exponential factor (*A*) (Figure 3b). The activation entropy (ΔS^{0*}) is reflected by the pre-exponential factor; therefore, based on transition state theory [55], ΔS^{0*} can be calculated from the kinetic data. While the energy barrier from the ground state to the transition state is quantified by *E_a*, the molecular freedom loss during the adsorption process is reflected by ΔS^{0*} . The compensation effect between *E_a* and ΔS^{0*} , as observed in Figure 3c, indicates that minimal reaction energy barriers are exhibited by catalysts featuring maximal freedom loss upon substrate adsorption (e.g., Pt@MIP-206-OH), thereby leading to maximal reaction rates. Given that methanol activation is recognized to be the key factor influencing the reaction rate in methanolysis of ammonia borane [56], the methanol adsorption should be of great importance. Since the loss of degrees of freedom upon substrate adsorption on the metal surface is closely related to the metal-substrate interaction strength, the Pt-methanol adsorption strength can be indicated by ΔS^{0*} . An attempt has been made to correlate ΔS^{0*} with TOF, and a strong linear relationship is found (Figure 3d), indicating that the reaction activity is determined by the adsorption strength between Pt and the substrate. Despite the above ideal results, due to the difficulty of directly customizing and experimentally measuring ΔS^{0*} in catalyst design, using ΔS^{0*} as a descriptor for catalytic activity remains unfeasible.

Therefore, a parameter related to the catalyst structure is sought that could be linked to the adsorption strength between metal center and substrate. Given that the only variable is the electron-donating capacity of the MOFs, a close relationship is assumed to exist between the electron transfer from the MOFs to Pt surface and the adsorption of substrates on Pt. To verify this hypothesis, the parameter Δe is attempted to correlate with ΔS^{0*} , and delightedly, a nearly linear relationship is observed (Figure 4a). This result indicates that the difference in ΔS^{0*} during the reaction is caused by the electron transfer (Δe) between the MOFs and Pt, suggesting that Δe can be regarded as a predictor of the Pt-methanol adsorption strength. Conventional XPS and CO-DRIFTS techniques were also employed for quantitative analysis (Figure S20). Although the parameters obtained from these techniques exhibit directional correlations with ΔS^{0*} , their linearity is relatively weak. These results suggest that XPS and CO-DRIFTS can serve as directional predictors of catalytic reactivity, whereas the XANES-derived Δe demonstrates a more prominent advantage in quantitatively describing the electronic modulation of Pt species.

Temperature-programmed desorption infrared spectroscopy (TPD-IR) of methanol over Pt@MIP-206-X (X = OH, OCH₃,

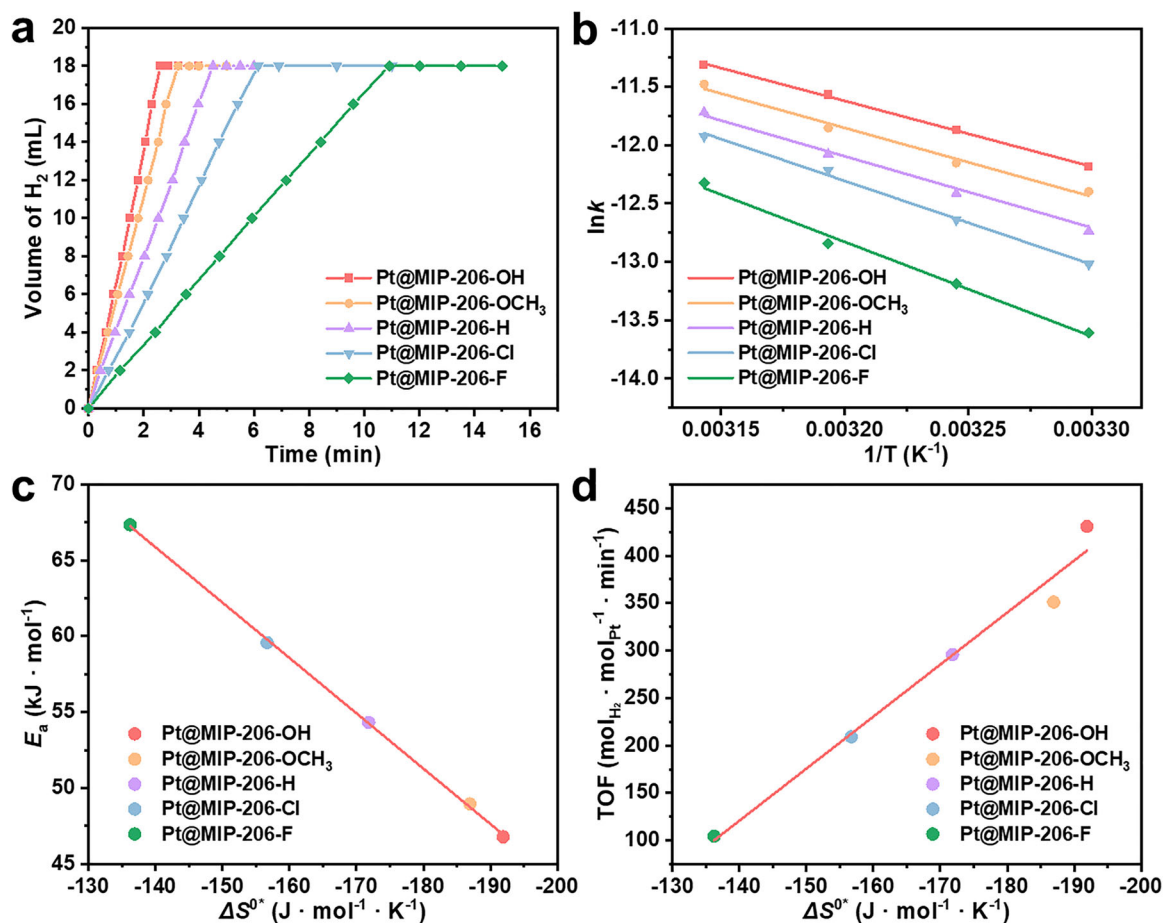


FIGURE 3 | (a) Catalytic activity of H₂ generation from the methanolysis of ammonia borane over Pt@MIP-206-X (X = OH, OCH₃, H, Cl, and F). (b) Arrhenius plots for the methanolysis of ammonia borane over Pt@MIP-206-X. (c) Correlations between E_a and ΔS[‡], and (d) Correlations between TOF and ΔS[‡] for the methanolysis of ammonia borane over Pt@MIP-206-X.

H, Cl, and F) have been collected to further demonstrate the feasibility of Δ*e* as a descriptor of Pt-methanol adsorption strength. The interaction strength between methanol and Pt can be inferred from the methanol desorption temperatures on Pt NPs, where higher temperatures indicate stronger adsorbate-surface interactions [57]. Initially, the TPD-IR spectra of methanol on MIP-206-H and Pt@MIP-206-H are compared (Figure S21). MIP-206-H shows a distinct absorption band at ~2842 cm⁻¹, which can be assigned to the symmetric stretching vibration of the -CH₃ group in methanol [58]. This peak is nearly eliminated upon heating to 120°C, indicating that methanol desorption on the MOF is largely complete at this temperature. In contrast, Pt@MIP-206-H exhibits a pronounced peak at ~2825 cm⁻¹, which can be assigned to the symmetric stretching vibration of -CH₃ in CH₃O*, formed via the dissociative adsorption of methanol. The presence of this peak confirms that methanol is dissociatively adsorbed on Pt, generating CH₃O* and H*, both of which remain adsorbed on the Pt surface. This characteristic band disappears at ~290°C, suggesting that the desorption temperature of CH₃O* on Pt lies near this temperature.

Similar vibrational features corresponding to dissociative methanol adsorption are also observed for the other Pt@MIP-206-X composites (Figure S22). The CH₃O* desorption temperature can be determined from the band disappearance. Based on the

previous analysis, Δ*e* is expected to be closely related to the methanol desorption. Therefore, Δ*e* was tried to correlate with the measured desorption temperature, and the results showcase a strong linear relationship (Figure 4a), further demonstrating that Δ*e* ideally describes the Pt-methanol adsorption strength.

Considering the excellent capability of Δ*e* in describing the Pt-methanol adsorption strength, the correlation between Δ*e* and TOF is further investigated. As expected, an excellent linear relationship is observed between them (Figure 4b). This conclusion is promising and encourages further investigations into the impact of catalyst structures on their reaction mechanisms. Isotopic labeling experiments are employed to investigate the O–H bond dissociation of methanol over Pt@MIP-206-X. By replacing CH₃OH with CH₃OD, the kinetic isotope effect (KIE) values for Pt@MIP-206-OH, Pt@MIP-206-OCH₃, Pt@MIP-206-H, Pt@MIP-206-Cl, and Pt@MIP-206-F are determined to be 3.47, 3.75, 3.91, 4.76, and 5.86, respectively (Figure S23 and Table S3). The pronounced KIE values for all samples confirm the O–H bond cleavage as the universal rate-determining step (RDS), according to the previous Ru-catalyzed methanolysis of ammonia borane [56]. A smaller KIE indicates that the step is more likely to occur [59, 60]. Therefore, Δ*e* was tried to correlate with the KIE of each catalyst, revealing an inverse correlation with a high degree of linearity (Figure 4b). It has been established that, when metal

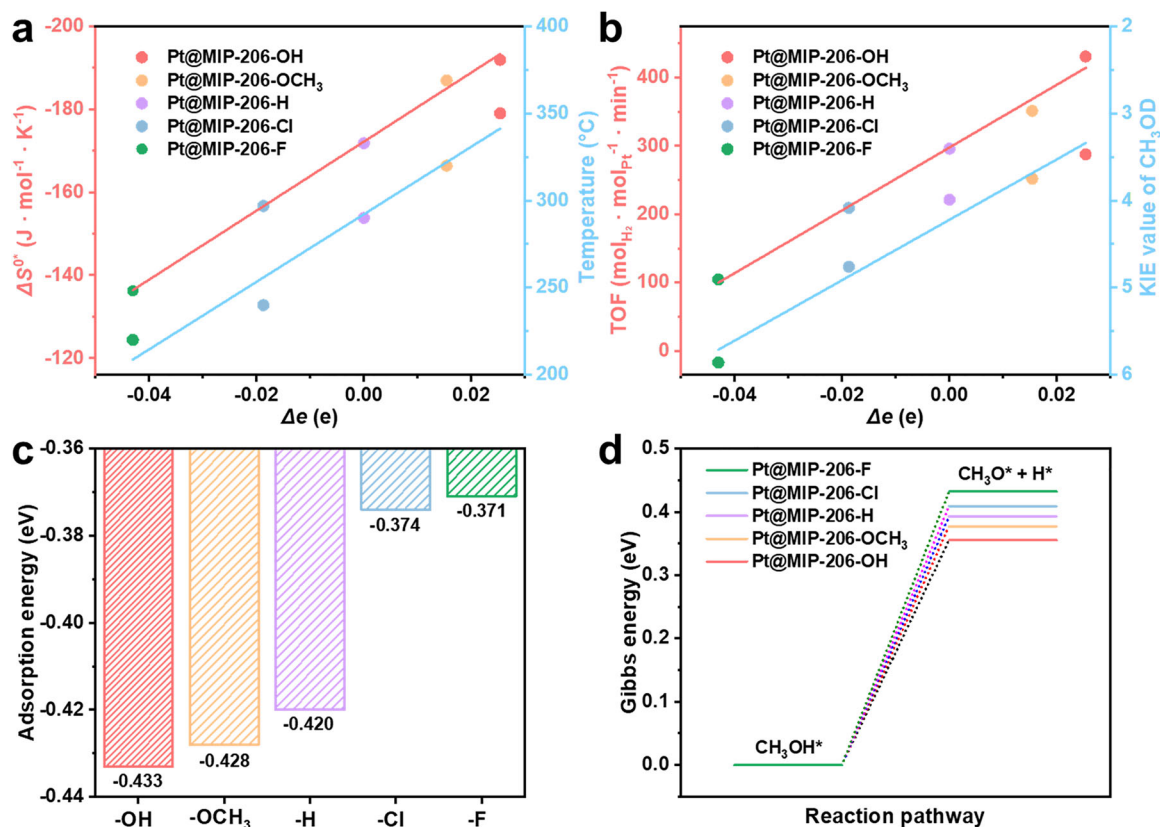


FIGURE 4 | (a) Correlations between Δe and ΔS^{0*} (red line) or methanol desorption temperature (blue line) in the methanolysis of ammonia borane over Pt@MIP-206-X (X = OH, OCH₃, H, Cl, and F). (b) Correlations between Δe and TOF (red line) or KIE (blue line) in the methanolysis of ammonia borane over Pt@MIP-206-X. (c) The calculated adsorption energies of methanol on Pt@MIP-206-X. (d) Free energy diagrams of methanol dehydrogenation over Pt@MIP-206-X.

center enhances the adsorption of O in methanol, the O–H bond cleavage becomes easy [61]. It can thus be inferred that MOFs with strong electron-donating ability (Δe) effectively increase the electron density of Pt, enhancing its adsorption of methanol, which in turn facilitates O–H bond cleavage and ultimately leads to improved activity.

Density functional theory (DFT) calculations have been further conducted to evaluate the influence of functional groups on methanol activation over MIP-206-X (X = OH, OCH₃, H, Cl, and F). The distance between the Pt NPs and the MOF pore walls was reasonably estimated based on the size of Pt NPs and the MOF pore dimensions, from which a simplified computational model is constructed. Given the structural complexity of the MOF-metal

NPs interface, the model may not fully capture all features of the real system. The charge transfer between Pt and MIP-206-X skeletons is quantified. Bader charge analysis reveals that the calculated Pt charge difference (ΔQ) for Pt@MIP-206-X (X = OH, OCH₃, H, Cl, and F) is 0.055, 0.030, -0.068, -0.182, and -0.194 e, respectively (Figures S24 and S25). In our definition, a positive ΔQ signifies charge accumulation on the framework. This confirms that maximal charge accumulation occurs in Pt@MIP-206-OH, which is consistent with the above experimental results. Adsorption energy calculations identify that Pt@MIP-206-OH as optimal for methanol adsorption (-0.433 eV) (Figures 4c and S26). The simulated Gibbs free energy change (ΔG) for methanol dehydro-

genation displays the O–H bond dissociation energies of 0.355, 0.377, 0.393, 0.409, and 0.432 eV, respectively for Pt@MIP-206-X (X = OH, OCH₃, H, Cl, and F) (Figures 4d and S27). Collectively, DFT calculations indicate that electrons can be transferred from MOFs with strong electron-donating ability to the Pt surface, leading to the enhancement of Pt's methanol adsorption strength and the reduction of dehydrogenation barriers, thus boosting catalytic activity, which is consistent with experimental results.

3 | Conclusion

In summary, five isorecticular MOFs with diverse functional groups have been synthesized and adopted to encapsulate Pt NPs with similar sizes and loadings, yielding Pt@MIP-206-X (X = OH, OCH₃, H, Cl, and F). This provides an ideal platform with the charge transfer between MOFs and Pt as the only variable affecting catalytic performance. The electron transfer between the MOFs and Pt is quantified with the descriptor Δe , which has been demonstrated to exhibit a linear correlation with the Pt-methanol adsorption strength (quantified by ΔS^{0*} and methanol desorption temperature) as well as the catalytic activity in ammonia borane methanolysis. Both experimental and computational results support that the higher the charge transfer from MOFs to Pt, the stronger the Pt-methanol adsorption, which promotes O–H bond cleavage and leads to enhanced activity. This study is unprecedented to quantify the charge transfer between

surrounding microenvironment and metal centers, proposing an experimentally accessible descriptor and establishing a quantitative relationship between metal electronic structure and catalytic activity, which is expected to be extended to small-sized metal cluster systems; this provides valuable insights into the design and synthesis of high-performance heterogeneous catalysts.

Author Contributions

Weidong Zhang: data curation, investigation, formal analysis, writing – original draft, writing – review and editing, methodology. **Jiajia Huang:** software, data curation, investigation, formal analysis, writing – review and editing. **Ruichao Xu:** software, methodology, data curation, investigation, validation, formal analysis, writing – review and editing. **Wentao Han:** data curation, formal analysis, writing – review and editing. **Mingyang Shen:** data curation, formal analysis, writing – review and editing. **Zhongyuan Lin:** visualization, writing – review and editing. **Jing-Yao Liu:** software, investigation, writing – review and editing. **Zhihu Sun:** software, methodology, formal analysis, writing – review and editing, project administration, supervision, resources. **Hai-Long Jiang:** conceptualization, formal analysis, supervision, resources, writing – review and editing, project administration.

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Conflicts of Interest

The authors declare no conflicts of interest

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. L. Zhang, M. Zhou, A. Wang, and T. Zhang, "Selective Hydrogenation Over Supported Metal Catalysts: From Nanoparticles to Single Atoms," *Chemical Reviews* 120 (2020): 683–733, <https://doi.org/10.1021/acs.chemrev.9b00230>.
2. G. Pacchioni and H. J. Freund, "Controlling the Charge state of Supported Nanoparticles in Catalysis: Lessons From Model Systems," *Chemical Society Reviews* 47 (2018): 8474–8502, <https://doi.org/10.1039/C8CS00152A>.
3. D. Leybo, U. J. Etim, M. Monai, S. R. Bare, Z. Zhong, and C. Vogt, "Metal-Support Interactions in Metal Oxide-Supported Atomic, Cluster, and Nanoparticle Catalysis," *Chemical Society Reviews* 53 (2024): 10450–10490, <https://doi.org/10.1039/D4CS00527A>.
4. C. Singhvi, G. Sharma, R. Verma, et al., "Tuning the Electronic Structure and SMSI by Integrating Trimetallic Sites With Defective Ceria for the CO₂ Reduction Reaction," *PNAS* 122 (2025): e2411406122, <https://doi.org/10.1073/pnas.2411406122>.
5. M. Hattori, N. Okuyama, H. Kurosawa, and M. Hara, "Low-Temperature Ammonia Synthesis on Iron Catalyst With an Electron

Donor," *Journal of the American Chemical Society* 145 (2023): 7888–7897, <https://doi.org/10.1021/jacs.2c13015>.

6. Y. Xie, J. Chen, J. Wen, et al., "Overturning CO₂ Hydrogenation Selectivity by Tailoring the Local Electron Density of Ru/CeO₂ Catalysts," *ACS Catalysis* 14 (2024): 12214–12224, <https://doi.org/10.1021/acscatal.4c03094>.
7. J. K. Nørskov, T. Bligaard, J. Rossmeisl, and C. H. Christensen, "Towards the Computational Design of Solid Catalysts," *Nature Chemistry* 1 (2009): 37–46, <https://doi.org/10.1038/nchem.121>.
8. B. Hammer and J. K. Nørskov, "Why Gold Is the Noblest of all the Metals," *Nature* 376 (1995): 238–240, <https://doi.org/10.1038/376238a0>.
9. X. Chang, Z. J. Zhao, Z. Lu, et al., "Designing Single-site Alloy Catalysts Using a Degree-of-isolation Descriptor," *Nature Nanotechnology* 18 (2023): 611–616, <https://doi.org/10.1038/s41565-023-01344-z>.
10. L. Wen, K. Sun, X. Liu, W. Yang, L. Li, and H. L. Jiang, "Electronic State and Microenvironment Modulation of Metal Nanoparticles Stabilized by MOFs for Boosting Electrocatalytic Nitrogen Reduction," *Advanced Materials* 35 (2023): 2210669, <https://doi.org/10.1002/adma.202210669>.
11. L. Jiao, J. Wang, and H. L. Jiang, "Microenvironment Modulation in Metal–Organic Framework-Based Catalysis," *Accounts of Materials Research* 2 (2021): 327–339, <https://doi.org/10.1021/accountsmr.1c00009>.
12. J. Chen, M. Jiang, F. Zhang, L. Wang, and J. Yang, "Interstitial Boron Atoms in Pd Aerogel Selectively Switch the Pathway for Glycolic Acid Synthesis From Waste Plastics," *Advanced Materials* 36 (2024): 2401867, <https://doi.org/10.1002/adma.202401867>.
13. Y. Zhang, G. Liu, L. Bian, et al., "Metal-Oxide Nanotube Channel Microenvironment Inducing Strong Metal-Oxide Interplay: A Case Study With CO₂ Hydrogenation to Methanol," *ACS Catalysis* 15 (2025): 15334–15349, <https://doi.org/10.1021/acscatal.5c01936>.
14. C. Li, Z. Wang, Y. Jin, et al., "Tunable Catalytic Vertex Wall Chemistry in Metal-Free Covalent Organic Frameworks for Enhanced Oxygen Reduction," *Angewandte Chemie International Edition* 64 (2025): e202500336, <https://doi.org/10.1002/anie.202500336>.
15. R. G. Rao, R. Blume, M. T. Greiner, et al., "Oxygen-Doped Carbon Supports Modulate the Hydrogenation Activity of Palladium Nanoparticles Through Electronic Metal–Support Interactions," *ACS Catalysis* 12 (2022): 7344–7356, <https://doi.org/10.1021/acscatal.2c01063>.
16. J. Wang, J. Yang, J. L. Wardini, et al., "Fermi Level Equilibration and Charge Transfer at the Exsolved Metal-Oxide Interface," *Journal of the American Chemical Society* 147 (2025): 2991–2997, <https://doi.org/10.1021/jacs.4c14695>.
17. J. Greeley, J. K. Nørskov, and M. Mavrikakis, "Electronic Structure and Catalysis on Metal Surfaces," *Annual Review of Physical Chemistry* 53 (2002): 319–348, <https://doi.org/10.1146/annurev.physchem.53.100301.131630>.
18. J. Dean, M. G. Taylor, and G. Mpourmpakis, "Unfolding Adsorption on Metal Nanoparticles: Connecting Stability With Catalysis," *Science Advances* 5 (2019): eaax5101, <https://doi.org/10.1126/sciadv.aax5101>.
19. P. P. Albertini, J. C. Mora, M. Guskova, et al., "Active Sites Under Electronic Effect Are More Sensitive to Microenvironment in CO₂ Electrorreduction," *Journal of the American Chemical Society* 147 (2025): 25517–25526, <https://doi.org/10.1021/jacs.5c05697>.
20. W. Chen, J. Cao, J. Yang, et al., "Molecular-level Insights Into the Electronic Effects in Platinum-catalyzed Carbon Monoxide Oxidation," *Nature Communications* 12 (2021): 6888, <https://doi.org/10.1038/s41467-021-27238-z>.
21. S. L. Nauert, L. Savereide, and J. M. Notestein, "Role of Support Lewis Acid Strength in Copper-Oxide-Catalyzed Oxidative Dehydrogenation of Cyclohexane," *ACS Catalysis* 8 (2018): 7598–7607, <https://doi.org/10.1021/acscatal.8b00935>.
22. N. Golio, I. Sen, X. Yu, P. Kondratyuk, and A. J. Gellman, "H₂–D₂ Exchange Activity and Electronic Structure of Ag_xPd_{1–x} Alloy Catalysts

- Spanning Composition Space,” *ACS Catalysis* 14 (2024): 11014–11025, <https://doi.org/10.1021/acscatal.4c02309>.
23. Y. Sun, Y. Cao, L. Wang, et al., “Gold Catalysts Containing Interstitial Carbon Atoms Boost Hydrogenation Activity,” *Nature Communications* 11 (2020): 4600, <https://doi.org/10.1038/s41467-020-18322-x>.
24. J. Wang, H. Y. Tan, C. S. Hsu, et al., “Adapting Atomic Configuration Steers Dynamic Half-Occupied State for Efficient CO₂ Electroreduction to CO,” *Journal of the American Chemical Society* 147 (2025): 13027–13038, <https://doi.org/10.1021/jacs.5c03121>.
25. X. Wang, X. J. Gao, L. Qin, et al., “eg Occupancy as an Effective Descriptor for the Catalytic Activity of Perovskite Oxide-based Peroxidase Mimics,” *Nature Communications* 10 (2019): 704, <https://doi.org/10.1038/s41467-019-08657-5>.
26. J. Simböck, M. Ghiasi, S. Schönebaum, U. Simon, F. M. F. de Groot, and R. Palkovits, “Electronic Parameters in Cobalt-Based Perovskite-Type Oxides as Descriptors for Chemocatalytic Reactions,” *Nature Communications* 11 (2020): 652, <https://doi.org/10.1038/s41467-020-14305-0>.
27. K.-I. Shimizu, T. Oda, Y. Sakamoto, Y. Kamiya, H. Yoshida, and A. Satsuma, “Quantitative Determination of Average Rhodium Oxidation state by a Simple XANES Analysis,” *Applied Catalysis B: Environment* 111–112 (2012): 509–514, <https://doi.org/10.1016/j.apcatb.2011.11.002>.
28. J. L. Vincent and P. A. Crozier, “Atomic Level Fluxional Behavior and Activity of CeO₂-supported Pt Catalysts for CO Oxidation,” *Nature Communications* 12 (2021): 5789, <https://doi.org/10.1038/s41467-021-26047-8>.
29. X. Du, Y. Huang, X. Pan, et al., “Size-dependent Strong Metal-support Interaction in TiO₂ Supported Au Nanocatalysts,” *Nature Communications* 11 (2020): 5811, <https://doi.org/10.1038/s41467-020-19484-4>.
30. H. Furukawa, K. E. Cordova, M. O’Keeffe, and O. M. Yaghi, “The Chemistry and Applications of Metal–Organic Frameworks,” *Science* 341 (2013): 1230444, <https://doi.org/10.1126/science.1230444>.
31. H.-C. J. Zhou and S. Kitagawa, “Metal–Organic Frameworks (MOFs),” *Chemical Society Reviews* 43 (2014): 5415–5418, <https://doi.org/10.1039/C4CS90059F>.
32. X. Zhao, Y. Wang, D. S. Li, X. Bu, and P. Feng, “Metal–Organic Frameworks for Separation,” *Advanced Materials* 30 (2018): 1705189, <https://doi.org/10.1002/adma.201705189>.
33. R. B. Lin, Z. Zhang, and B. Chen, “Achieving High Performance Metal–Organic Framework Materials Through Pore Engineering,” *Accounts of Chemical Research* 54 (2021): 3362–3376, <https://doi.org/10.1021/acs.accounts.1c00328>.
34. L. Jiao and H. L. Jiang, “Metal-organic Frameworks for Catalysis: Fundamentals and Future Prospects,” *Chinese Journal of Catalysis* 45 (2023): 1–5, [https://doi.org/10.1016/S1872-2067\(22\)64193-7](https://doi.org/10.1016/S1872-2067(22)64193-7).
35. G. Li, S. Zhao, Y. Zhang, and Z. Tang, “Metal–Organic Frameworks Encapsulating Active Nanoparticles as Emerging Composites for Catalysis: Recent Progress and Perspectives,” *Advanced Materials* 30 (2018): 1800702, <https://doi.org/10.1002/adma.201800702>.
36. L. Li, Z. Li, W. Yang, et al., “Integration of Pd Nanoparticles With Engineered Pore Walls in MOFs for Enhanced Catalysis,” *Chemistry* 7 (2021): 686–698, <https://doi.org/10.1016/j.chempr.2020.11.023>.
37. K. L. Kollmannsberger, L. Kronthaler, J. R. Jinschek, and R. A. Fischer, “Defined Metal Atom Aggregates Precisely Incorporated Into Metal–organic Frameworks,” *Chemical Society Reviews* 51 (2022): 9933–9959, <https://doi.org/10.1039/D1CS00992C>.
38. M. Mukoyoshi and H. Kitagawa, “Nanoparticle/Metal–organic Framework Hybrid Catalysts: Elucidating the Role of the MOF,” *Chemical Communications* 58 (2022): 10757–10767, <https://doi.org/10.1039/D2CC03233C>.
39. Q. Yang, Q. Xu, and H. L. Jiang, “Metal–organic Frameworks Meet Metal Nanoparticles: Synergistic Effect for Enhanced Catalysis,” *Chemical Society Reviews* 46 (2017): 4774–4808, <https://doi.org/10.1039/C6CS00724D>.
40. J. Chen, Y. Wang, F. Wang, and Y. Li, “Photo-Induced Switching of CO₂ Hydrogenation Pathway Towards CH₃OH Production Over Pt@UiO-66-NH₂(Co),” *Angewandte Chemie International Edition* 62 (2023): e202218115, <https://doi.org/10.1002/anie.202218115>.
41. C. Fang, L. Liu, J. Weng, et al., “Modifiers versus Channels: Creating Shape-Selective Catalysis of Metal Nanoparticles/Porous Nanomaterials,” *Angewandte Chemie International Edition* 60 (2021): 976–982, <https://doi.org/10.1002/anie.202011866>.
42. K. M. Choi, K. Na, G. A. Somorjai, and O. M. Yaghi, “Chemical Environment Control and Enhanced Catalytic Performance of Platinum Nanoparticles Embedded in Nanocrystalline Metal–Organic Frameworks,” *Journal of the American Chemical Society* 137 (2015): 7810–7816, <https://doi.org/10.1021/jacs.5b03540>.
43. A. Aijaz, A. Karkamkar, Y. J. Choi, et al., “Immobilizing Highly Catalytically Active Pt Nanoparticles inside the Pores of Metal–Organic Framework: A Double Solvents Approach,” *Journal of the American Chemical Society* 134 (2012): 13926–13929, <https://doi.org/10.1021/ja3043905>.
44. S. Hu, C. Xie, Y. P. Xu, et al., “Selectivity Control in the Direct CO Esterification Over Pd@UiO-66: The Pd Location Matters,” *Angewandte Chemie International Edition* 62 (2023): e202311625, <https://doi.org/10.1002/anie.202311625>.
45. X. Li, T. W. Goh, L. Li, et al., “Controlling Catalytic Properties of Pd Nanoclusters Through Their Chemical Environment at the Atomic Level Using Isorecticular Metal–Organic Frameworks,” *ACS Catalysis* 6 (2016): 3461–3468, <https://doi.org/10.1021/acscatal.6b00397>.
46. S. Wang, L. Chen, M. Wahiduzzaman, et al., “A Mesoporous Zirconium-Isophthalate Multifunctional Platform,” *Matter* 4 (2021): 182–194, <https://doi.org/10.1016/j.matt.2020.10.009>.
47. H. Wang, X. Zhang, W. Zhang, M. Zhou, and H. L. Jiang, “Heteroatom-Doped Ag₂₅ Nanoclusters Encapsulated in Metal–Organic Frameworks for Photocatalytic Hydrogen Production,” *Angewandte Chemie International Edition* 63 (2024): e202401443, <https://doi.org/10.1002/anie.202401443>.
48. L. Liu, M. Lopez-Haro, C. W. Lopes, et al., “Structural Modulation and Direct Measurement of Subnanometric Bimetallic PtSn Clusters Confined in Zeolites,” *Nat Catal* 3 (2020): 628–638, <https://doi.org/10.1038/s41929-020-0472-7>.
49. M. Xu, X. Qin, Y. Xu, et al., “Boosting CO Hydrogenation towards C₂₊ Hydrocarbons Over Interfacial TiO_{2-x}/Ni Catalysts,” *Nature Communications* 13 (2022): 6720, <https://doi.org/10.1038/s41467-022-34463-7>.
50. N. Cheng, S. Stambula, D. Wang, et al., “Platinum Single-atom and Cluster Catalysis of the Hydrogen Evolution Reaction,” *Nature Communications* 7 (2016): 13638, <https://doi.org/10.1038/ncomms13638>.
51. A. N. Mansour, J. W. Cook Jr., and D. E. Sayers, “Quantitative Technique for the Determination of the Number of Unoccupied D-electron States in a Platinum Catalyst Using the L_{2,3} X-ray Absorption Edge Spectra,” *Journal of Physical Chemistry* 88 (1984): 2330–2334, <https://doi.org/10.1021/j150655a029>.
52. Y. Chen, J. Lin, L. Li, et al., “Identifying Size Effects of Pt as Single Atoms and Nanoparticles Supported on FeO X for the Water-Gas Shift Reaction,” *ACS Catalysis* 8 (2018): 859–868, <https://doi.org/10.1021/acscatal.7b02751>.
53. Q. Xu and M. Chandra, “Catalytic Activities of Non-noble Metals for Hydrogen Generation From Aqueous Ammonia–borane at Room Temperature,” *Journal of Power Sources* 163 (2006): 364–370, <https://doi.org/10.1016/j.jpowsour.2006.09.043>.
54. R. J. Madon and M. Boudart, “Experimental Criterion for the Absence of Artifacts in the Measurement of Rates of Heterogeneous Catalytic Reactions,” *Industrial and Engineering Chemistry Fundamentals* 21 (1982): 438–447, <https://doi.org/10.1021/i100008a022>.

55. L. Liu and Q. X. Guo, "Isokinetic Relationship, Isoequilibrium Relationship, and Enthalpy–Entropy Compensation," *Chemical Reviews* 101 (2001): 673–696, <https://doi.org/10.1021/cr990416z>.
56. X. Li, Q. Yao, Z. Li, H. Li, Q. L. Zhu, and Z. H. Lu, "Porphyrin Framework-derived N-doped Porous Carbon-confined Ru for NH_3BH_3 Methanolysis: The More Pyridinic-N, the Better," *Journal of Materials Chemistry A* 10 (2022): 326–336, <https://doi.org/10.1039/D1TA06807E>.
57. L. DeRita, S. Dai, K. Lopez-Zepeda, et al., "Catalyst Architecture for Stable Single Atom Dispersion Enables Site-Specific Spectroscopic and Reactivity Measurements of CO Adsorbed to Pt Atoms, Oxidized Pt Clusters, and Metallic Pt Clusters on TiO_2 ," *Journal of the American Chemical Society* 139 (2017): 14150–14165, <https://doi.org/10.1021/jacs.7b07093>.
58. T. Chen, Z. Feng, G. Wu, et al., "Mechanistic Studies of Photocatalytic Reaction of Methanol for Hydrogen Production on Pt/ TiO_2 by in Situ Fourier Transform IR and Time-Resolved IR Spectroscopy," *Journal of Physical Chemistry C* 111 (2007): 8005–8014, <https://doi.org/10.1021/jp071022b>.
59. W. Liu, J. Jiang, Z. Li, et al., "Effective Hole Utilization for Atomically Dispersed Low-Coordination Molybdenum Accelerating Photocatalytic C–H Activation," *Angewandte Chemie International Edition* 64 (2025): e202507312, <https://doi.org/10.1002/anie.202507312>.
60. L. Zhang, R. Chen, Y. Tu, et al., "Revealing the Crystal Facet Effect of Ceria in Pd/ CeO_2 Catalysts Toward the Selective Oxidation of Benzyl Alcohol," *ACS Catalysis* 13 (2023): 2202–2213, <https://doi.org/10.1021/acscatal.2c04252>.
61. W. Tu and Y. H. Chin, "Catalytic Consequences of the Thermodynamic Activities at Metal Cluster Surfaces and Their Periodic Reactivity Trend for Methanol Oxidation," *Angewandte Chemie International Edition* 53 (2014): 12148–12152, <https://doi.org/10.1002/anie.201405232>.

Supporting Information

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