

Gold-MOF Catalysis: Synthesis, Classification and Catalytic Reactions

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Abstract. Gold catalysts have attracted extensive research attention owing to their distinctive π -Lewis acidity and catalytic performance, yet their practical applications are severely restricted by poor thermal stability and severe agglomeration tendency. Metal-organic frameworks (MOFs) feature ordered pore channels and tunable chemical environments, which serve as an ideal platform to stabilize gold species via spatial confinement and coordination interactions. This review summarizes the research advances of Au-MOF materials. Three preparation strategies are categorized, namely in-situ synthesis, post-synthetic modification, as well as core-shell structure and encapsulation strategy, with in-depth commentary on their respective merits and drawbacks. Meanwhile, the catalytic applications of Au-MOF catalysts in various reactions are discussed, including alcohol oxidation, CO oxidation, photoreduction of CO₂, N₂ activation and alkyne activation. Special attention is paid to the performance differences between gold nanoparticles and gold nanoclusters, and the synergistic effect between MOF matrix and gold species is elaborated. Finally, the design directions for high-efficiency and stable Au-MOF catalysts are prospected, and current challenges including atomic-level precise control and large-scale production are also discussed.

Keywords: Au-catalyst, MOF, Synthesis, Catalysis

1. Introduction

Benefiting from its inert electronic structure and chemical stability, gold ranks among the most stable elemental metals, and has long been regarded as a metal with extremely low catalytic activity throughout history. Nevertheless, revolutionary progress has been achieved in the research of gold catalysts over the past decades, completely reversing researchers' traditional understanding of its catalytic activity. Since the late 1990s, with the deepening research on homogeneous gold catalysis, various Au_i or Au_{iii} complexes have been developed one after another, exhibiting unique π -Lewis acidity capable of efficiently activating unsaturated substrates such as alkynes, alkenes and allenes [1, 2]. In parallel, substantial progress has been made in the ligand structural design and catalyst synthesis of gold catalysts—from early phosphine ligands to the widely concerned N-heterocyclic carbene (NHC) ligands in recent years. Such complexes deliver catalytic performance superior to traditional gold complex systems in cycloisomerization, hydrofunctionalization, oxidative coupling and other reactions [3-5]. At the nanoscale, gold also displays unique catalytic properties. Driven by

aurophilic interactions, gold readily agglomerates into sub-nanometer clusters (AuNCs). Such materials draw intensive attention due to their discrete electronic energy levels, huge specific surface area and distinctive quantum size effect [6-11].

However, the application of gold catalysts faces critical bottlenecks: insufficient thermal stability leads to agglomeration and deactivation under catalytic conditions; additionally, irreversible structural collapse occurs after ligand dissociation, resulting in loss of active sites [12, 13]. How to achieve effective stabilization while retaining their unique catalytic performance has become a core urgent issue to be solved in this field. The synthesis and development of Metal-Organic Framework (MOF) materials provide a solution to the above challenges. Since Yaghi's group first synthesized carboxylic acid-linked MOF materials in 1995, such crystalline porous materials self-assembled by metal nodes and organic ligands via coordination bonds have undergone rapid development [14-16]. Compared with traditional inorganic porous materials (e.g., zeolites, activated carbon), MOFs possess outstanding structural designability and functional tunability. The pore size, shape and chemical environment can be precisely regulated by rational selection of metal nodes and organic ligands [17, 18]. These characteristics endow MOFs with broad application prospects in gas storage and separation, sensing, drug delivery, catalysis and other fields [19, 20].

More importantly, the ordered pore channels of MOFs provide ideal confined space for stabilizing gold atoms and gold clusters [21, 22]. By encapsulating gold species within MOF pore channels or anchoring them onto frameworks, spatial confinement effects generated by pore channels, cage cavities or open metal sites in MOF skeletons can effectively prevent migration and agglomeration of gold species at high temperatures, maintain their high dispersion state and thus remarkably extend service life. Furthermore, residual groups on MOF surfaces, such as nitrogen-, oxygen- and sulfur-containing coordination sites, act as "trapping sites" to form strong electrostatic interactions with gold species, preventing leaching of active components in liquid phase. Notably, MOFs are not merely "containers" supporting gold species. The synergistic effect between MOFs and gold clusters can modulate the electronic structure of catalytic active centers, and even generate brand-new catalytic properties unavailable for single components [23, 24]. For instance, Bai et al. constructed AuNCs@UiO-68 composites via coordination interactions between DNA-templated gold clusters and zirconium-based MOFs. Studies reveal that the confinement effect of MOFs not only greatly enhances the oxidase-mimicking activity of gold clusters, but also significantly improves their structural stability [25]. These studies fully demonstrate the unique advantages of MOFs as stabilizing carriers for gold clusters, offering new ideas for developing high-performance gold-based catalysts.

In summary, gold-centered MOF materials (including gold complex-modified MOFs, gold cluster@MOF composites and gold-node MOFs) possess broad development prospects and application value. Focusing on Au-MOF catalytic systems, this review systematically discusses their synthetic strategies, structural features and catalytic performance, with emphasis on research advances and catalytic mechanism studies in organic molecule activation, small molecule activation and A³-coupling reactions. By summarizing current research status and key challenges in this field, this work provides favorable guidance for the future development of more efficient and stable Au-MOF catalytic materials.

2. Synthetic methods and binding modes of Au-MOFs

2.1. Controllable synthetic strategies

At present, numerous studies focus on highly dispersing gold single atoms or nanoparticles onto MOF skeletons. Conventional approaches include solvothermal method, microwave-assisted method, sonochemical method, mechanochemical method, electrochemical method, etc. These methods disperse gold particulates into MOFs via external physical and chemical means, with corresponding characteristics and applicability summarized in the table below:

Table 1. Comparison of characteristics and applicability of gold-MOF composites prepared by different synthesis methods

Synthetic Method	Core Characteristics	Applicability	References
Solvothermal Method	Most classical, high crystallinity; morphology controllable via modulators	Widely applicable, the first choice for most MOF materials	[26, 27]
Microwave Assisted Method	Rapid nucleation, short reaction duration	Rapid synthesis of nanosized MOF particles	[28-30]
Sonochemical Method	Mild conditions, uniform nucleation	Thermally sensitive systems or biocomposite systems	[31, 32]
Mechanochemical Method	Large-scale production, solvent-free or low solvent conditions	Low crystallinity yet environmentally friendly	[33]
Electrochemical Method	Continuous synthesis, high yield	Thin film fabrication or industrial production	[34]

According to the timing and mode of gold species introduction, three major strategies are available for fabricating gold-MOF materials: in-situ synthesis strategy, post-synthetic modification strategy, as well as core-shell structure and encapsulation strategy.

The in-situ synthesis strategy introduces gold species simultaneously during MOF synthesis to realize one-pot preparation. Specifically, gold precursors such as HAuCl_4 are mixed with other metal salts and organic ligands in the reaction system, followed by in-situ reduction or coordination during MOF crystallization to obtain MOF materials [27]. Though straightforward, this method faces the difficulty of matching gold reduction rate with MOF crystallization rate. To control gold reduction rate, microwave assistance can accelerate uniform nucleation of the system, or sonochemical treatment facilitates precursor dispersion and nucleation under mild conditions to avoid damage to gold coordination environments at high temperatures. For certain MOF preparations, solvent-free mechanochemical synthesis can be adopted to obtain final products via solid-state grinding of reactants. This approach suits thermally sensitive gold complex precursors, yet the resulting materials generally exhibit low crystallinity [33].

The post-synthetic modification strategy first synthesizes gold-free MOF frameworks, then introduces gold species through chemical transformation. Its core logic lies in incorporating gold into preformed MOFs. This method is widely adopted in current research on gold-containing MOFs due to simple operation and favorable retention of MOF crystallinity and porosity. For example, pre-synthesized MOFs are immersed in HAuCl_4 solution, followed by reduction after trivalent gold diffuses into MOF pores [35, 36]. During this process, ultrasonic assistance enables rapid reduction to generate gold nanoparticles inside pore channels, while electrochemical deposition achieves directional gold deposition via precise potential control. Nevertheless, attention should be paid that

high gold loading may lead to gold nanoparticle formation merely on MOF surfaces, or oversized internal nanoparticles triggering collapse of MOF skeletons.

The core-shell structure and encapsulation strategy first synthesizes gold species, then induces heterogeneous nucleation of MOF materials on their surfaces via surface modification to realize protection and size control of gold species, with its priority placed on surface functionalization. After surface functionalization, MOF thin films can be deposited via solvothermal or electrochemical methods. Compared with the former two strategies, this method enables fabrication of MOF materials with gold as linking organic ligand skeletons [37].

The above three synthetic strategies have distinct focuses and applicable scenarios: in-situ synthesis features simple operation and one-pot fabrication; post-synthetic modification imposes minimal damage to frameworks and helps maintain MOF crystallinity and porosity; core-shell encapsulation achieves precise size control and comprehensive protection of gold species. Researchers can flexibly select strategies according to structural requirements of target materials and application scenarios. However, synthetic methods only serve as implementation approaches for material construction. The interfacial interaction between gold species and MOF skeletons constitutes the core essence for maintaining high dispersion of gold species and preventing agglomeration-induced deactivation. Clarifying their bonding modes and stabilization mechanisms not only guides optimization of synthetic routes, but also provides theoretical basis for directional regulation of subsequent catalytic activity.

2.2. Bonding modes between gold species and MOFs

Diverse bonding interactions exist between gold species and MOFs. In accordance with hard and soft acid-base theory, gold belongs to soft acids, so most species capable of forming coordination bonds with it are soft bases, typically thioethers or NHC ligands. An attractive design idea is to introduce specific functional groups (e.g., thiols, oximes) into MOF pore channels or skeletons during material design, which generate strong coordination interactions with trivalent gold to stabilize gold species.

Another strategy introduces redox-active sites into MOF materials. Adsorption of gold ions is accompanied by reduction of trivalent gold, and the generated gold nanoparticles are immobilized within MOFs via framework confinement or coordination interactions with MOF skeletons. This adsorption-reduction-immobilization process realizes efficient capture of gold ions and encapsulation of gold particles [38].

The "locking effect" also acts as an effective strategy to stabilize gold nanoparticles. This strategy "locks" MOF carriers through aldehyde-amine condensation reactions, followed by metal salt adsorption and reduction. Such a method can effectively adjust metal charge and drastically improve the catalytic activity of metal centers in reactions [39].

Innovation in synthetic methods and analysis of interfacial interaction mechanisms ultimately serve the enhancement of catalytic performance. Relying on spatial confinement, pore screening and metal-support synergistic effects of MOFs, Au-MOF composite materials exhibit superior activity, selectivity and cycling stability compared with traditional supported gold catalysts in various catalytic reactions. Based on the scale and structural characteristics of active gold species, Au-MOF catalytic systems can be classified into two categories: gold nanoparticle catalysis and gold nanocluster catalysis. The former boasts mature fabrication processes and wide applicable reaction scenarios, while the latter features atomically precise structures and unique electronic properties, offering possibilities for in-depth analysis of catalytic mechanisms and precise regulation of performance. This chapter systematically sorts out research advances of both systems in typical

catalytic reactions, and discusses their catalytic characteristics and action mechanisms combined with specific reaction systems.

3. Classification of catalytic reactions over Au-MOFs

3.1. Gold nanoparticle catalysis

3.1.1. Alcohol oxidation reactions

Conversion of alcohol hydroxyl groups to carbonyl groups represents one of the most important reactions in organic synthesis. Although a series of reagents have been developed to oxidize primary alcohols into aldehydes and secondary alcohols into ketones in the past, stoichiometric chromate and similar reagents produce massive ecologically polluting waste. Therefore, oxidation using molecular oxygen meets the requirements of green chemistry better.

In 2009, Tsunoyama's group first reported the activity of small-sized Au/polyvinylpyrrolidone in alcohol oxidation reactions, proving gold nanoclusters to be excellent catalysts for alcohol oxidation. Subsequently, reports emerged on gold nanoparticles supported on MgO and CeO₂ for alcohol oxidation. Such carriers not only improve the dispersion and thermal stability of gold nanoparticles, but also modulate surface electronic structures via strong metal-support interactions, significantly enhancing activation capacity toward molecular oxygen [40, 41].

In 2021, Zhu's group proposed hollow nanoparticle@MOF core-shell structures capable of simultaneously utilizing the confinement effect of hollow nanoparticles and the high specific surface area plus tunable pore advantages of MOFs. Meanwhile, the group developed a one-step strategy to construct hollow Au@Zn/Ni-MOF₂ core-shell porous structures. The hollow core-shell architecture was obtained via molecular-level structural transformation of pre-synthesized solid Au@Zn/Ni-MOF₂. Hollow cavities facilitate mass transfer, while the outer Zn/Ni-MOF₂ shell stabilizes gold nanoparticles and realizes size-selective recognition of substrates. In the catalytic oxidation of benzyl alcohol, this MOF material delivers higher turnover frequency than gold nanoparticles supported on other media, achieving over 98% yield and above 99% selectivity within 2 hours. This originates from its larger specific surface area, lower density and superior mass transfer performance under identical conditions [42].

In 2022, Wen's group reported Au-Pd nanoparticles embedded within ultrathin MOF nanosheets for efficient catalysis of benzyl alcohol oxidation. The team noticed synergistic effects between metal nanoparticles on ultrathin Ni-based MOF nanosheets (NMOF-Ni), and anticipated that introduction of Au and Pd atoms into NMOF-Ni could raise conversion and selectivity of benzyl alcohol oxidation. After testing different Au-Pd ratios, Au₂Pd₁@NMOF-Ni displayed extremely high catalytic performance. XPS analysis of electronic states indicated that Au-Pd interactions alter their electronic structures and effectively enhance surface electronegativity. In benzyl alcohol oxidation, the system reached 99% yield after 9 hours with a turnover frequency of 30.7 h⁻¹. The ultrathin nanosheets expose abundant active sites owing to small thickness and effectively promote reaction progress. Reports point out that β -hydrogen elimination of alcohols constitutes the rate-determining step, and strong bimetallic synergism facilitates β -hydrogen elimination [43].

3.1.2. CO oxidation

Catalytic carbon monoxide oxidation stands as one of the most classic reactions for gold-containing MOF materials. In 2009, Xu's group loaded organic gold complexes onto ZIF-8 metal-organic

frameworks via solid-state grinding, followed by hydrogen reduction to prepare Au@ZIF-8 catalysts. Such catalysts realize repeatable CO oxidation catalysis from room temperature to 315–340 °C. This report is regarded as a landmark early study on MOF-confined gold catalysis [44].

In 2013, Huang's group explored a novel universal, simple and efficient colloidal method to match the size of MOFs and metal nanoparticles. HAuCl₄ was adopted as gold precursor, and oleylamine provided mild reduction conditions to stabilize generated gold nanoparticles, separating the nucleation and growth processes of gold nanoparticles to form monodispersed nanoparticles. Compared with solution impregnation and other approaches, this method features simpler procedures. Meanwhile, the catalyst exhibits favorable performance in catalytic carbon monoxide oxidation, efficiently converting CO within a wide temperature range [45].

In 2018, Xu's team proposed a fabrication route for metal/quasi-MOF composites via partial deligandization of metal/MOF composites. Pre-synthesized Au/MIL-101 metal-organic framework materials were calcined at high temperatures, accompanied by deligandization of gold nanoparticles. Precise temperature control yields partially deligandized quasi-MOF materials with retained Au/MIL-101 porosity and intact structures. Such quasi-MOF materials possess more exposed active sites and thus deliver higher activity in CO oxidation. Complete CO conversion was achieved at 193 K, 253 K, 273 K and 298 K, and 100% CO conversion was maintained for 4000 minutes at 193 K, demonstrating outstanding catalytic activity and stability [46].

3.1.3. CO₂ activation

Photocatalytic carbon dioxide reduction constitutes an eco-friendly reaction consistent with green chemistry demands, hence numerous studies focus on utilizing MOF catalysts to photoreduce CO₂ into CO, CH₄, CH₃OH and other organic products. The mechanism of photocatalytic CO₂ reduction comprises five distinct stages: first, CO₂ and reducing agents are adsorbed onto catalyst surfaces. Subsequently, upon light absorption, electrons (e⁻) and holes (h⁺) are generated in the conduction band (CB) and valence band (VB) of semiconductors. Such charge carriers then migrate to catalyst surfaces and interact with adsorbed species such as CO₂. Finally, reaction products desorb from catalyst surfaces, restarting the cycle with adsorption of new reactants [47]. Studies show that accelerating photoelectron migration rates on MOF surfaces can effectively boost CO₂ reduction rates.

When combined with semiconductors, gold nanoparticles act as photoelectron reservoirs, driving accumulation of photoelectrons on gold nanoparticle surfaces to realize multi-electron reduction of CO₂. In addition, gold nanoparticles exhibit strong absorption across the visible spectrum due to localized surface plasmon resonance (LSPR) effects, improving light capture capacity and overall photocatalytic efficiency of photocatalysts [48].

In 2019, Duan's group noted that MOFs feature tunable structures and clear active sites as photocatalysts for CO₂ reduction, yet two drawbacks exist: slow CO₂ mass transfer inside micropores and low light absorption efficiency caused by encapsulated light-harvesting units. Two-dimensional porphyrin-based MOFs were designed with layered structures, and gold nanoparticles were loaded onto nanosheet surfaces via electrostatic interactions to overcome the above limitations. Gold nanoparticles amplify local electric fields, raise local CO concentrations generated by photoreduction, increase surface photocurrent and reduce impedance. Modulation of MOF nanosheet thickness and assembly modes of supported AuNPs improves charge transfer and mass transport efficiency during photocatalytic CO₂ reduction, elevating light absorption and catalytic efficiency [49].

In 2024, Xu's group designed and fabricated a novel zirconium/titanium bimetallic oxide solid solution $\text{Ti}_x\text{Zr}_{1-x}\text{O}_2$ loaded with gold nanoparticles via post-synthetic modification and MOF derivatization. Adjusting gold doping modes controls the distribution of metal species in such MOF-derived materials. Strong interactions exist between gold particles and the bimetallic oxide solid solution system. Ti doping into ZrO_2 effectively narrows the band gap of this semiconductor material and promotes photocatalytic performance. Supported by the solid solution, Au/TZO displays strong adsorption of the key intermediate $^*\text{COOH}$ during reduction, while the energy barrier for C-C coupling is lower than that of heterojunctions, proving the potential of this catalyst in CO_2 reductive coupling [48].

3.1.4. Nitrogen reduction

Traditional plasma photocatalytic nitrogen fixation generally adopts a coupling mode of "plasma antenna (Au/Ag) + semiconductor co-catalyst", yet this pathway faces three major bottlenecks: (1) Schottky barriers hinder transfer of hot electrons from plasma nanoparticles to semiconductors, lowering photoelectric conversion efficiency; (2) remote catalytic centers lie far from transient confined LSPR fields and fail to fully utilize plasma effects for direct activation of N_2 molecules; (3) extremely low solubility and slow mass transfer of N_2 in aqueous solutions severely restrict reaction rates at gas-liquid-solid three-phase interfaces. To address the above issues, Chen et al. reported a direct plasma photocatalytic nitrogen fixation strategy based on Au@UiO-66. Optically inert UiO-66 was selected as matrix, and ultra-small gold nanoparticles were encapsulated within MOF cages via impregnation-reduction methods. The high porosity and water stability of UiO-66 effectively prevent agglomeration of Au NPs and guarantee accessibility of N_2 molecules and hydrated protons to gold active sites. Different from traditional architectures, each gold nanoparticle serves as both photosensitizer and catalytic center in this system. Upon visible light excitation, hot electrons generated by LSPR directly reduce N_2 molecules without semiconductor mediation. Meanwhile, LSPR-induced energy transfer and local electric field polarization synergistically activate $\text{N}\equiv\text{N}$ bonds, drastically lowering the energy barrier of the rate-determining step ($\text{N}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{NNH}$). To further break the N_2 mass transfer limit, gas-membrane-solution three-phase reaction interfaces were designed to allow N_2 gas to diffuse directly through MOF membranes to regions adjacent to gold active sites, rather than relying on slow dissolution-diffusion processes in solutions. This design raises ammonia yield by approximately 2.5 times compared with traditional powder suspension systems (PiS), while enabling convenient separation and recycling of catalysts. This work first realized direct plasma nitrogen fixation independent of semiconductor co-catalysts in Au-MOF systems, providing conceptual verification for MOF-confined gold catalysis of small molecule activation. Research on Au-MOFs for direct photo/electrocatalytic N_2 reduction remains in its initial stage, and this work stands as a landmark report in this field [50].

3.1.5. Alkyne activation reactions

Analogous to small-molecule gold catalysts acting as excellent alkyne activators, gold embedded within MOFs participates in alkyne activation. As solid-phase materials, Au-MOFs exhibit more convenient post-treatment compared with homogeneous small-molecule gold catalysts. Nevertheless, only a limited number of catalytic reaction reports on gold-MOFs have been published to date, listed below to inspire follow-up research filling gaps in this field.

Among reported reactions, three-component condensation of paraformaldehyde, secondary amines and aryl alkynes to synthesize propargylamines finds wide applications in pharmaceutical

fields. In 2017, Wang's group addressed two drawbacks of traditional two-step fabrication of gold nanoparticle-supported metal-organic frameworks: structural damage to MOFs and poor size control of gold nanoparticles. Microwave irradiation accelerated rapid crystallization, completing synthesis of MOF materials loaded with ultra-fine gold nanoparticles within merely two minutes, with gold loading up to 5.13% and average gold nanoparticle size below 2 nm. This catalyst delivers high turnover numbers and turnover frequencies in the three-component condensation reaction generating propargylamine derivatives, accompanied by negligible gold leaching during catalysis and unnoticeable performance decay after five recycling cycles [51].

In 2018, Jiang's group resolved previous disputes over whether $\text{Au}^{\delta+}$ or Au^0 constitutes the active gold site in three-component reactions. MOFs containing imine and hydroxyl groups were designed to coordinate and anchor gold species of two distinct oxidation states. Since MIL-101-SA- Au^0 containing Au^0 was obtained via one-step reduction of MIL-101-SA- $\text{Au}^{\delta+}$, the only difference lies in gold oxidation states. Experiments verified that the catalytic activity of MIL-101-SA- $\text{Au}^{\delta+}$ is 11 times that of MIL-101-SA- Au^0 , confirming $\text{Au}^{\delta+}$ as the more efficient catalytic center [52].

Furthermore, two studies published in 2021 and 2023 modified amino groups on UiO-66- NH_2 MOF skeletons with biguanide or aminotetrazole groups. Modified MOFs generate stronger coordination effects toward gold nanoparticles, enabling catalysis of three-component condensation reactions under mild conditions with high turnover frequencies and stability [53, 54].

In recent years, several reports have applied gold-MOF systems to classic coupling reactions of alkynes. For instance, Dong's group reported bimetallic N-heterocyclic carbene complexes catalyzing tandem alkyne hydration-Suzuki coupling reactions in 2021 to resolve poor redox compatibility of multi-catalytic systems. The porous network formed by metal ions and organic ligands in MOF materials allows introduction of different supported metal catalysts with identical coordination functions, presenting distinct activation modes and realizing novel reactivity unavailable for single-component catalysts. The group incorporated gold and palladium heterocyclic bis-carbene species into UiO-67 MOFs, where synergistic interactions between two metal sites promote tandem alkyne hydration-Suzuki coupling reactions. The catalyst can be reused for at least six cycles without obvious loss of catalytic activity, and delivers favorable yields for a series of carbon-bromine bond-containing substrates, demonstrating good functional group compatibility [55].

In summary, gold nanoparticle@MOF systems have been extensively validated across alcohol oxidation, CO oxidation, CO_2 reduction, nitrogen reduction, alkyne activation and other reactions, exhibiting outstanding stability and substrate size selectivity as the mainstream research system in current Au-MOF catalysis. When gold species shrink from nanoscale to sub-nanometer clusters or even atomically precise clusters, discrete electronic energy levels and unique quantum size effects generate entirely distinct catalytic behaviors. The ordered pore channels and tunable microenvironments of MOFs provide ideal confined space for precise construction and stabilization of gold nanoclusters, giving rise to a new class of cluster-based catalytic materials with distinctive performance.

3.2. Gold nanocluster catalysis

3.2.1. Regulation of Au cluster structures via MOF confinement

(1) Size Confinement and Atomic-Number Precise Control

Ordered pore channels of MOFs act as natural "nanoreactors" for gold clusters, restricting the upper growth limit of clusters via pore size adjustment. Rebel et al. introduced volatile $\text{Au}(\text{CO})\text{Cl}$

precursors into HKUST-1 pore channels via vapor infiltration, utilizing water ligands on Cu sites within pores to induce hydrolysis and decomposition of precursors, successfully preparing Au_x clusters with an average atomic number $x \approx 5$, and ToF-SIMS mass spectrometry detected cluster distribution extending to Au_7 . Notably, such clusters exhibit crystallographically ordered distribution within MOF pore channels, and PXRD simulations confirm their uniform dispersion in mesopores, reflecting strict size confinement effects of MOF pore channels on clusters [56].

(2) Electronic Structure Regulation

Beyond physical spatial confinement, MOF metal nodes and organic ligands interact electronically with gold clusters to modulate their surface electronic structures. For example, confinement of ultra-fine gold nanoclusters within Cu-doped ZIF-8 nanorod arrays enables Cu doping sites to alter surface electronic states of gold clusters, facilitating formation of gold hydride intermediates and further exerting remarkable impacts on catalytic selectivity [57]. Such a "dual regulation mechanism of confinement-ligand" indicates that MOF skeletons are not inert containers, but active components participating in constructing the final electronic structures of clusters.

3.2.2. Catalytic reactions and applications

MOF confinement not only provides structurally stable "nanoreactors" for gold clusters, but pore wall chemical environments can further modulate electronic states of clusters to significantly influence catalytic performance. A representative work from University of Science and Technology of China encapsulated atomically precise $Au_{25}(Capt)_{18}$ clusters into a series of functionalized UiO-66 ($UiO-66-X$, $X = H, NH_2, OH, NO_2$). Spatial confinement effects of MOFs suppress migration and agglomeration of clusters after surface ligand removal, successfully obtaining clean-surface Au_{25} clusters. In the oxidative esterification of furfural, this series of catalysts displays drastically different activity from free Au_{25} clusters and surface-supported clusters on MOFs: Au_{25} confined within $UiO-66-NH_2$ delivers optimal catalytic performance, while clusters confined within $UiO-66-NO_2$ show the lowest activity. Experiments and theoretical calculations prove that pendant functional groups on MOF pore walls systematically regulate electronic structures of Au_{25} clusters via electron-donating/electron-withdrawing effects—the electron-donating amino group elevates d-electron density of Au_{25} and optimizes adsorption energy of furfural substrates, whereas the electron-withdrawing nitro group weakens substrate adsorption. This work first demonstrates synergistic regulation of metal nanoclusters via MOF spatial confinement and pore wall chemical engineering, establishing a new paradigm of "dual regulation of confinement-microenvironment" for rational design of high-performance cluster catalysts [58].

4. Conclusion

In conclusion, gold-metal-organic framework composite catalytic systems break through the application bottleneck of easy agglomeration and deactivation of traditional gold catalysts relying on spatial confinement effects, tunable pore microenvironments of MOFs and synergistic interactions between gold and skeletons, exhibiting excellent catalytic performance and structural stability in multiple reaction systems including alcohol oxidation, CO oxidation, CO_2 photoreduction, nitrogen reduction and alkyne activation. At present, researchers have developed various preparation strategies such as in-situ synthesis, post-synthetic modification and core-shell encapsulation, and preliminarily revealed stabilization and activation mechanisms including size confinement and electronic regulation. Nevertheless, numerous challenges remain in this field: universal methods for atomic-level precise controllable synthesis of gold species under high loading are still lacking;

dynamic evolution and structure-activity relationships of active centers under real reaction conditions require more in-situ characterizations and theoretical verification; large-scale preparation and long-cycle performance for industrial applications demand further exploration. In the future, with continuous advances in synthetic chemistry, in-situ characterization technologies and theoretical calculations, Au-MOF catalytic materials are expected to achieve more breakthroughs in precise design of active sites, quantitative elucidation of catalytic mechanisms and expansion of application scenarios, providing additional new possibilities for the development of heterogeneous gold catalysis and construction of green chemical processes.

References

- [1] Hashmi, A. S. K., Hutchings, G. J. (2006). Gold catalysis. *Angewandte Chemie International Edition*, 45, 7896–7936.
- [2] Dorel, R., Echavarren, A. M. (2015). Gold(I)-catalyzed activation of alkynes for the construction of molecular complexity. *Chemical Reviews*, 115, 9028–9072.
- [3] Nolan, S. P. (2011). The development and catalytic uses of N-heterocyclic carbene gold complexes. *Accounts of Chemical Research*, 44, 91–100.
- [4] Ansari, E., Khan, M. A., Sharma, R., et al. (2026). The evolving landscape of gold(I)-NHC chemistry: Synthesis, characterization, and catalytic activity. *Coordination Chemistry Reviews*, 549, 217314.
- [5] Gorin, D. J., Sherry, B. D., Toste, F. D. (2012). Ligand effects and ligand design in homogeneous gold(I) catalysis. *Journal of the American Chemical Society*, 134, 5697–5705.
- [6] Jin, R., Zeng, C., Zhou, M., et al. (2016). Atomically precise colloidal metal nanoclusters and nanoparticles: Fundamentals and opportunities. *Chemical Reviews*, 116, 10346–10413.
- [7] Pan, X., Yao, Y., Zhang, M., et al. (2024). Enzyme-mimic catalytic activities and biomedical applications of noble metal nanoclusters. *Nanoscale*, 16, 8196–8215.
- [8] Zhu, M., Aikens, C. M., Hollander, F. J., et al. (2008). Correlating the crystal structure of a thiol-protected Au₂₅ cluster and optical properties. *Journal of the American Chemical Society*, 130, 5883–5885.
- [9] Alkhursani, S. A., Aldaleeli, N. Y., Al-Gahtany, S. A., et al. (2024). Future prospects of gold nanoclusters in hydrogen storage systems and sustainable environmental treatment applications. *Nanotechnology Reviews*, 13, 20240087.
- [10] Hossain, S., Hirayama, D., Ikeda, A., et al. (2023). Atomically precise thiolate-protected gold nanoclusters: Current status of designability of the structure and physicochemical properties. *Aggregate*, 4, e255.
- [11] Negishi, Y., Kurashige, W., Niihori, Y., et al. (2013). Toward the creation of stable, functionalized metal clusters. *Physical Chemistry Chemical Physics*, 15, 18736–18751.
- [12] Fang, J., Zhang, B., Yao, Q., et al. (2018). Recent advances in the synthesis and catalytic applications of ligand-protected, atomically precise metal nanoclusters. *Coordination Chemistry Reviews*, 369, 76–93.
- [13] Kawawaki, T., Kataoka, Y., Hirata, M., et al. (2021). Creation of high-performance heterogeneous photocatalysts by controlling ligand desorption and particle size of gold nanocluster. *Angewandte Chemie International Edition*, 60, 21510–21520.
- [14] Yaghi, O. M., & Li, H. (1995). Hydrothermal synthesis of a metal-organic framework containing large rectangular channels. *Journal of the American Chemical Society*, 117, 10401–10402.
- [15] Li, H., Eddaoudi, M., O’Keeffe, M., et al. (1999). Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature*, 402, 276–279.
- [16] Moghadam, P. Z., Li, A., Wiggins, S. B., et al. (2017). Development of a Cambridge structural database subset: A collection of metal–organic frameworks for past, present, and future. *Chemistry of Materials*, 29, 2618–2625.
- [17] Farha, O. K., Eryazici, I., Jeong, N. C., et al. (2012). Metal–organic framework materials with ultrahigh surface areas: Is the sky the limit? *Journal of the American Chemical Society*, 134, 15016–15021.
- [18] Furukawa, H., Cordova, K. E., O’Keeffe, M., et al. (2013). The chemistry and applications of metal-organic frameworks. *Science*, 341, 1230444.
- [19] Abdelkareem, M. A., Abbas, Q., Sayed, E. T., et al. (2024). Recent advances on metal-organic frameworks (MOFs) and their applications in energy conversion devices: Comprehensive review. *Energy*, 299, 131127.
- [20] Zeggai, F. Z., Ait-Touchente, Z., Bachari, K., Elaissari, A. (2025). Investigation of metal-organic frameworks (MOFs): Synthesis, properties, and applications - An in-depth review. *Chemical Physics Impact*, 10, 100864.

- [21] Vilhelmsen, L. B., Walton, K. S., Sholl, D. S. (2012). Structure and mobility of metal clusters in MOFs: Au, Pd, and AuPd clusters in MOF-74. *Journal of the American Chemical Society*, 134, 12807-12816.
- [22] Li, B., Wen, H. M., Cui, Y., et al. (2016). Emerging multifunctional metal-organic framework materials. *Advanced Materials*, 28, 8819-8860.
- [23] Yang, Q., Xu, Q., Jiang, H. L. (2017). Metal-organic frameworks meet metal nanoparticles: Synergistic effect for enhanced catalysis. *Chemical Society Reviews*, 46, 4774-4808.
- [24] Liu, L., Corma, A. (2018). Metal catalysts for heterogeneous catalysis: From single atoms to nanoclusters and nanoparticles. *Chemical Reviews*, 118, 4981-5079.
- [25] Bai, P., Zhou, A., Xie, M., et al. (2025). Confinement effect of zirconium metal-organic frameworks derived enhanced oxidase-like activity and stability of gold nanoclusters for biosensing. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 337, 126153.
- [26] Stock, N., & Biswas, S. (2012). Synthesis of metal-organic frameworks (MOFs): Routes to various MOF topologies, morphologies, and composites. *Chemical Reviews*, 112, 933-969.
- [27] Li, H., Eddaoudi, M., Groy, T. L., et al. (1998). Establishing microporosity in open metal-organic frameworks: Gas sorption isotherms for Zn(BDC) (BDC = 1,4-benzenedicarboxylate). *Journal of the American Chemical Society*, 120, 8571-8572.
- [28] Pham, T. P., Hong, J., Tran, N., et al. (2023). The properties of microwave-assisted synthesis of metal-organic frameworks and their applications. *Nanomaterials*, 13, 352.
- [29] Li, L. (2025). Microwave synthesis in zeolite and MOF membranes. *Membranes*, 15, 275.
- [30] Jiang, B.-X., Wang, H., Zhang, Y.-T., et al. (2023). Microwave-assisted synthesis of Zr-based metal-organic frameworks and metal-organic cages. *Polyhedron*, 243, 116569.
- [31] Qiu, L.-G., Li, Z.-Q., Wu, Y., et al. (2008). Facile synthesis of nanocrystals of a microporous metal-organic framework by an ultrasonic method and selective sensing of organoamines. *Chemical Communications*, 44, 3642–3644.
- [32] Kallawar, G., Thakare, N., Bonde, S., et al. (2024). Exploring sonochemical synthesis for photocatalyst nanocomposites in water and wastewater treatment: An in-depth review. *Journal of Cleaner Production*, 485, 144279.
- [33] Beldon, P. J., Fabian, L., Stein, R. S., et al. (2010). Rapid room-temperature synthesis of zeolitic imidazolate frameworks by using mechanochemistry. *Angewandte Chemie International Edition*, 49, 9640–9643.
- [34] Guo, W., Han, N., Wang, S., et al. (2025). Anodic deposition of metal-organic framework films: From fundamentals to applications. *Coordination Chemistry Reviews*, 544, 216955.
- [35] Lazzarini, A., Colaiezzi, R., Gabriele, F., et al. (2021). Support-activity relationship in heterogeneous catalysis for biomass valorization and fine-chemicals production. *Materials*, 14, 6796.
- [36] Bedia, J., Muelas-Ramos, V., Penas-Garzon, M., et al. (2019). A review on the synthesis and characterization of metal organic frameworks for photocatalytic water purification. *Catalysts*, 9, 52.
- [37] Osterrieth, J. W. M., Wright, D., Noh, H., et al. (2019). Core-shell gold nanorod@zirconium-based metal-organic framework composites as in situ size-selective Raman probes. *Journal of the American Chemical Society*, 141, 3893–3900.
- [38] Xue, T., He, T., Peng, L., et al. (2023). A customized MOF-polymer composite for rapid gold extraction from water matrices. *Science Advances*, 9, 4923.
- [39] Zhong, Y., Liao, P., Li, G., et al. (2023). Locking effect in metal@MOF with superior stability for highly chemoselective catalysis. *Journal of the American Chemical Society*, 145, 22673–22681.
- [40] Kaneda, K., & Mitsudome, T. (2017). Metal-support cooperative catalysts for environmentally benign molecular transformations. *Chemical Record*, 17, 4–26.
- [41] Santra, C., Auroux, A., & Chowdhury, B. (2016). Bi doped CeO₂ oxide supported gold nanoparticle catalysts for the aerobic oxidation of alcohols. *RSC Advances*, 6, 45330–45342.
- [42] Qin, N., Pan, A., Yuan, J., et al. (2021). One-step construction of a hollow Au@bimetal-organic framework core-shell catalytic nanoreactor for selective alcohol oxidation reaction. *ACS Applied Materials & Interfaces*, 13, 12463–12471.
- [43] Guo, T., Bao, S., Guo, J., et al. (2022). Bimetallic Au-Pd NPs embedded in MOF ultrathin nanosheets with tuned surface electronic properties for high-performance benzyl alcohol oxidation. *Chemical Research in Chinese Universities*, 38, 1344–1348.
- [44] Jiang, H.-L., Liu, B., Akita, T., et al. (2009). Au@ZIF-8: CO oxidation over gold nanoparticles deposited to metal-organic framework. *Journal of the American Chemical Society*, 131, 11302–11303.
- [45] Wu, R., Qian, X., Zhou, K., et al. (2013). Highly dispersed Au nanoparticles immobilized on Zr-based metal-organic frameworks as heterostructured catalyst for CO oxidation. *Journal of Materials Chemistry A*, 1, 14294.

- [46] Tsumori, N., Chen, L., Wang, Q., et al. (2018). Quasi-MOF: Exposing inorganic nodes to guest metal nanoparticles for drastically enhanced catalytic activity. *Chem*, 4, 845–856.
- [47] Atta, M. R., Al-Mahmodi, A. F., Al-Dhawi, B. N. S., et al. (2025). MOF-based catalysts for CO₂ reduction via photo-, electro-, and photoelectrocatalysis: A review. *Academia Green Energy*, 2, 1.
- [48] Huang, N.-Y., Li, B., Wu, D., et al. (2024). Crystal engineering of MOF-derived bimetallic oxide solid solution anchored with Au nanoparticles for photocatalytic CO₂ reduction to syngas and C₂ hydrocarbons. *Angewandte Chemie International Edition*, 63, e202319177.
- [49] Chen, L., Wang, Y., Yu, F., et al. (2019). A simple strategy for engineering heterostructures of Au nanoparticle-loaded metal-organic framework nanosheets to achieve plasmon-enhanced photocatalytic CO₂ conversion under visible light. *Journal of Materials Chemistry A*, 7, 11355–11361.
- [50] Chen, L.-W., Hao, Y.-C., Guo, Y., et al. (2021). Metal-organic framework membranes encapsulating gold nanoparticles for direct plasmonic photocatalytic nitrogen fixation. *Journal of the American Chemical Society*, 143, 5727–5736.
- [51] Jiang, Y., Zhang, X., Dai, X., et al. (2017). Microwave-assisted synthesis of ultrafine Au nanoparticles immobilized on MOF-199 in high loading as efficient catalysts for a three-component coupling reaction. *Nano Research*, 10, 876–889.
- [52] Yang, Q., Jiang, H.-L. (2018). Oxidation or reduction state of Au stabilized by an MOF: Active site identification for the three-component coupling reaction. *Small Methods*, 2, 1800216.
- [53] Veisi, H., Sayadi, M., Morakabati, N., et al. (2022). Au NPs fabricated on biguanidine-modified Zr-UiO-66 MOFs: A competent reusable heterogeneous nanocatalyst in the green synthesis of propargylamines. *New Journal of Chemistry*, 46, 2829–2836.
- [54] Mohammadi, L., Taghavi, R., Hosseini, M., et al. (2023). Gold nanoparticle decorated post-synthesis modified UiO-66-NH₂ for A₃-coupling preparation of propargyl amines. *Scientific Reports*, 13, 9051.
- [55] Dong, Y., Li, W.-H., & Dong, Y.-B. (2021). Dual-metal N-heterocyclic carbene complex (M = Au and Pd)-functionalized UiO-67 MOF for alkyne hydration-Suzuki coupling tandem reaction. *Journal of Organic Chemistry*, 86, 1818–1826.
- [56] Hassan, Z. M., Guo, W., Welle, A., et al. (2023). Formation of gold nanoclusters from goldcarbonyl chloride inside the metal-organic framework HKUST-1. *Molecules*, 28, 2716.
- [57] Gao, G., Xi, Q., Zhang, Y., et al. (2019). Atomic-scale engineering of MOF array confined Au nanoclusters for enhanced heterogeneous catalysis. *Nanoscale*, 11, 1169–1176.
- [58] Wang, H., Liu, X., Zhao, Y., et al. (2024). Regulating interaction with surface ligands on Au₂₅ nanoclusters by multivariate metal-organic framework hosts for boosting catalysis. *National Science Review*, 11, nwae252.