

Rhythmical catalysis of Au₁₀ clusters for KA oil oxidation to ε-caprolactone

Xinyi Xu^{1,§}, Yining Zhang^{1,§}, Yiqi Tian¹, Hao Wang¹, Gongde Wu², Qiang Yuan¹, Shuhua Li¹✉, and Yan Zhu^{1,3}✉

¹ Key Laboratory of Mesoscopic Chemistry of Ministry of Education, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

² School of Environment Engineering, Nanjing Institute of Technology, Nanjing 211167, China

³ State Key Laboratory of Low Carbon Catalysis and Carbon Dioxide Utilization, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

[§] Xinyi Xu and Yining Zhang contributed equally to this work.

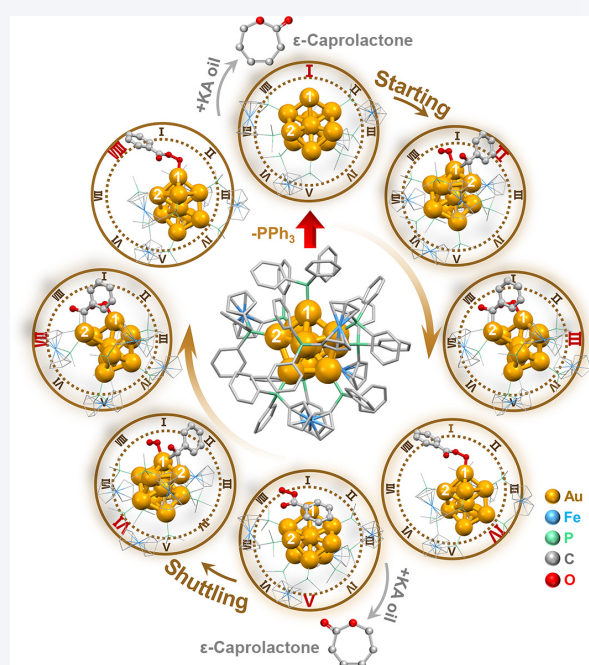
 Cite this article: Nano Research, 2026, 19, 94908863. <https://doi.org/10.26599/NR.2026.94908863>

ABSTRACT: Identifying active sites in heterogeneous catalysis has intrigued researches for many decades yet remains a challenge. This becomes more challenging to reveal the responsiveness of local sites on a catalyst to reactive species during a reaction. Here we utilize a flexible Au₁₀(DPPF)₄PPh₃ cluster to pinpoint active sites and untangle the communication between adjacent sites to match transient intermediates underlying the key steps from KA oil oxidation to ε-caprolactone. Our study suggests that the detachment of a triphenylphosphine ligand at the initial reaction exposes one Au atom and breaks one Au–Au bond on this cluster, thereby invoking two Au atoms to activate dioxygen and benzaldehyde to form benzoyl hydroperoxide intermediate. Sequentially, the two Au atoms spontaneously approach to adapt to the bridged adsorption of benzaldehyde over the two sites, leading to re-bonding of the two Au atoms and meanwhile stabilizing the cluster structure. More notably, the desorption of hydroperoxide intermediate from the active sites persuades this Au–Au bond to open again for being active sites in the next cycle. This interactive catalysis between active sites and reactants leads to benzoyl hydroperoxide affluently produced on the cluster to oxidize KA oil, eventually achieving a record-high synthesis efficiency for ε-caprolactone.

KEYWORDS: precise cluster, rhythmical catalysis, KA oil oxidation, flexibility, cooperation

1 Introduction

ε-Caprolactone (ε-CL) is a high-value monomer central to the production of biodegradable polyesters and advanced polymeric materials, widely used in environmental, agricultural and



biomedical applications [1–3]. Currently, the mainstream industrial production of ε-CL relies on Baeyer–Villiger oxidation of cyclohexanone with peracids (Fig. 1(a)), which suffers from limited selectivity (~ 85%), potential explosion risk, and high cost of stoichiometric oxidant [4–6]. More critically, cyclohexanone is typically derived from industrial KA oil (a mixture of cyclohexanol and cyclohexanone), requiring substantial nonproductive energy for multistep separation prior to oxidation [7, 8]. The direct conversion of unseparated KA oil to ε-CL using molecular oxygen as oxidant represents a preferable alternative. Previous efforts have been devoted to integrating the two discrete steps (alcohol dehydrogenation and Baeyer–Villiger oxidation) into a one-pot

Received: April 15, 2026; Revised: May 20, 2026

Accepted: May 21, 2026

✉ Address correspondence to Yan Zhu, zhuyan@nju.edu.cn; Shuhua Li, shuhua@nju.edu.cn

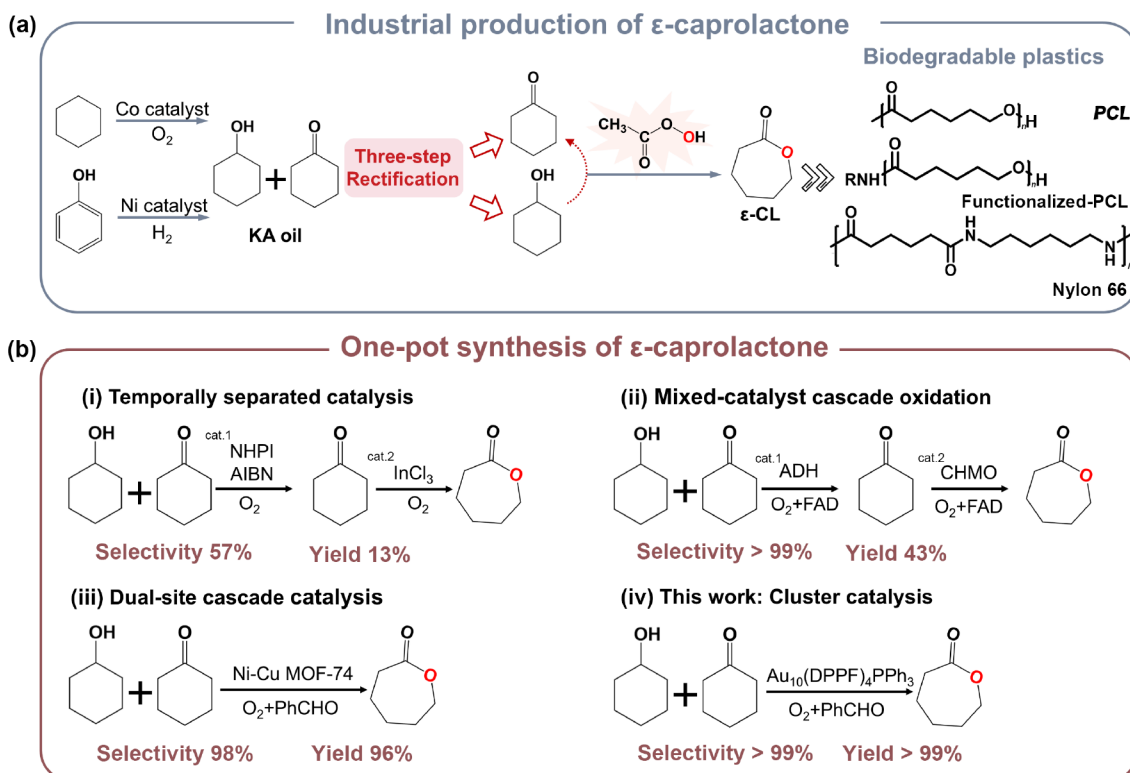


Figure 1 Different synthetic routes for ϵ -caprolactone: (a) industrial production route; (b) one-pot synthesis method. (i) Temporally separated oxidative process catalyzed by organometallic complex and metal; (ii) mixed catalytic system; (iii) dual-site cascade catalysis; (iv) cascade catalysis process catalyzed by atomically precise metal clusters reported in this work.

reaction system, including the spatially separated sequential catalyst system [9] or the mixed catalyst system [10]. However, limited success was achieved due to operational limitations, low selectivity, and poor productivity (Fig. 1(b)). Hence, one-step catalytic oxidation of KA oil on a single catalyst is a promising approach for the efficient production of ϵ -CL. For instance, Tang et al. [11] recently proposed a cascade oxidation strategy using O_2 and benzaldehyde under the catalysis of NiCu-MOF-74, demonstrating the feasibility of one-step conversion of KA oil to ϵ -CL, whereas the intrinsic reaction rate and catalytic efficiency remain suboptimal. Therefore, novel catalytic systems for the cascade oxidation of KA oil should be explored to improve the productivity of ϵ -CL under the premise of high selectivity.

With the aim of improving catalytic efficiency, the proportion of active sites that effectively participate in the reaction and continuously regenerate during the reaction is of vital importance [12–15]. In heterogeneous catalysis based on supported metal nanostructures, due to the broad size distributions and irregular morphology, only a small portion actually serve as active centers in the catalytic process. Such heterogeneity affects the efficient utilization of metal active sites, thereby reducing the selectivity and productivity toward target product [16, 17]. Therefore, the development of catalysts with well-defined active centers is necessary for improving the performance and understanding catalytic mechanisms. Accordingly, the precise metal cluster with crystallographic structure offers a promising opportunity and has attracted attention from heterogeneous and homogeneous catalysis fields [18–20]. These metal clusters typically consist of a well-defined metal core and various organic ligands shell, just like protein-encapsulated metal clusters of a few atoms bridged by the ligands. On the one hand, the uniformity and functional

differentiation of active sites in metal clusters maximize the utilization efficiency of metal atoms, as each site can be precisely defined and selectively engaged in specific elementary steps [21]. On the other hand, with well-defined metal cores and ligand environments, atomically precise metal clusters provide a unique platform to probe the structural evolution of active sites during catalysis, and to map up how local sites respond to reactive species exactly. More importantly, these systems combine structural integrity with tunable flexibility, permitting dynamic adaptation of active sites through coordination rearrangement and electronic redistribution. Such behavior closely resembles enzyme “induced-fit” mechanisms, which are essential for multistep transformations [22, 23]. Therefore, atomically precise metal clusters represent a powerful model system for developing high-performance catalysts for KA oil cascade oxidation, delivering both fundamental insights into catalytic origin and practical advantages in the efficient, selective, and controllable conversion.

In this work, we focus on catalytic applications of $Au_{10}(DPPF)_4PPh_3$ cluster catalyst for KA oil oxidation to produce ϵ -CL and explore the mutual adaptability of active sites and active species using the flexible atomic-precision structure. The Au_{10} catalyst achieved remarkable performance in the cascade oxidation, recording a high yield rate of $248 \text{ mol} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ with 100% selectivity for ϵ -CL, markedly superior to the reported catalysts. Our study reveals that the Au_{10} seamlessly integrates two distinct phosphine ligands of DPPF and PPh_3 , in which the weak coordinated PPh_3 ligands are prone to detachment and pre-organize available Au sites for substrate entry. Notably, the Au_{10} displays a rhythmic catalytic process, that the two Au atoms could undergo the tangible-intangible pendulum to activate dioxygen and benzaldehyde for the benzoyl hydroperoxide that is crucial oxygen

species for the KA oil oxidation, alternately accompanied with catalytic reactivity and structural stability. This cluster actively and frequently feeds back to reactive species for completing a cycle of the KA oil oxidation toward ϵ -CL, and then re-engineers itself to begin again for the next cycle, finally exhibiting a record performance.

2 Results and discussion

2.1 Total structure of Au_{10} cluster

As shown in Fig. 2(a), the total structure of $Au_{10}(DPPF)_4PPh_3$ cluster (hereafter Au_{10}) can be viewed as a 10-atom gold kernel capped by four bulky bidentate 1,1'-bis(diphenylphosphine) ferrocene (DPPF) and one monodentate triphenylphosphine (PPh_3), where an Au atom is located at the center and another nine Au atoms on the surface are coordinated by phosphines [24]. The cluster is quite unique, that is, both soft and robust, which is

presented in its flexible ability to handle changes of reactive species during the whole reaction. Specifically, DPPF, with its rigid ferrocene framework and strong chelating action, acts like a structural clamp, firmly stabilizing the clustered framework and suppressing structural distortion. Furthermore, its large steric hindrance further prevents complete surface passivation, thus creating a geometrically mismatched surface that exposes some metal sites. In contrast, the PPh_3 ligand binds to the more exposed Au-apex, exhibiting weaker coordination ability and readily dissociating under catalytic conditions, generating coordination-unsaturated active sites. Such an exceptional ligand arrangement establishes a balance between structural rigidity and dynamic accessibility [25, 26].

2.2 Catalytic performance for KA oil cascade oxidation

Based on the well-defined structure and good accessibility of Au_{10} cluster, we next sought to explore its catalytic performance in the oxidation of KA oil. As shown in Fig. 2(b), with oxygen as the

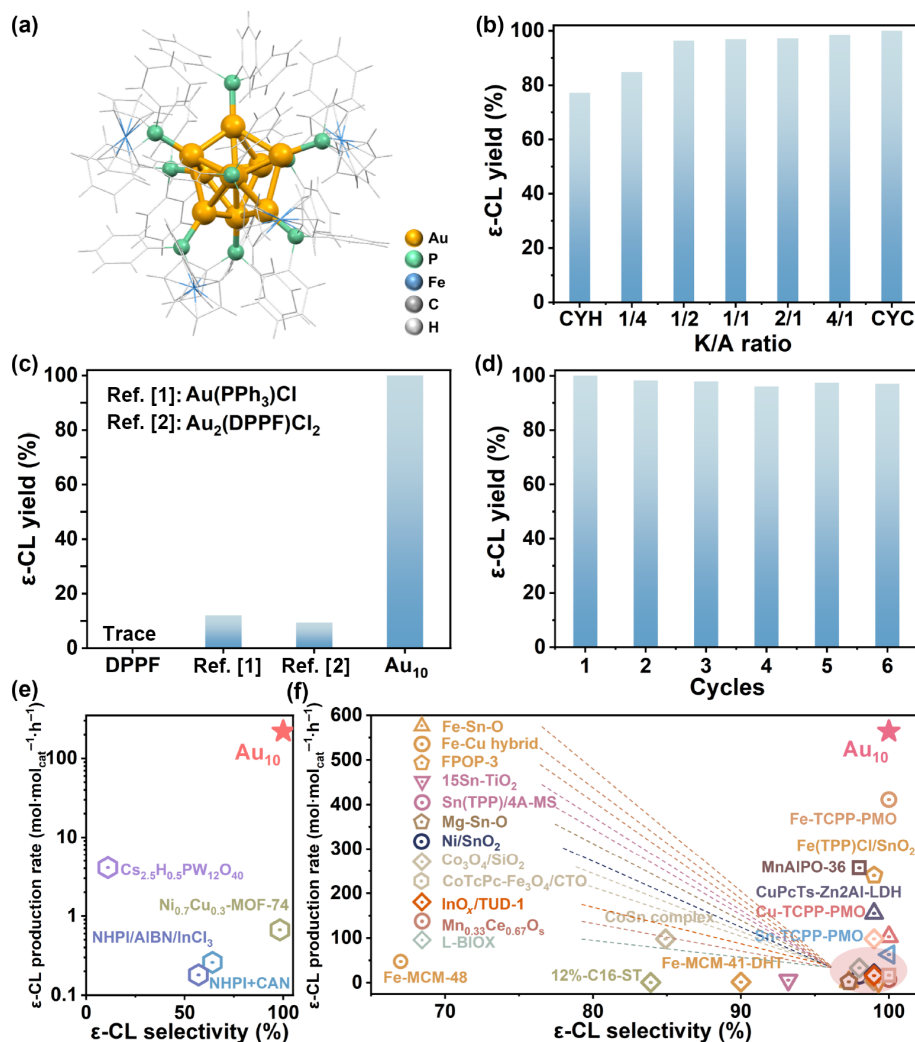


Figure 2 (a) Total structure of $Au_{10}(DPPF)_4PPh_3$ cluster. (b) Catalytic performances of KA oil oxidation under different K/A ratios over Au_{10} catalyst. Reaction conditions: 2 mg catalyst, 1.0 mmol substrate, $n(\text{benzaldehyde}) = n(\text{cyclohexanol}) \times 2.5 + n(\text{cyclohexanone}) \times 1.25$, 8 mL dichloroethane, 80 °C, 1 MPa O_2 , 12 h. (c) Catalytic performances of the oxidation of KA oil on the Au_{10} catalyst and other comparative catalysts. Reaction conditions: 1.0 mmol substrate (K/A ratio = 1/2), 2 mg catalyst, 2.1 mmol benzaldehyde, 8 mL dichloroethane, 80 °C, 1 MPa O_2 , 12 h. (d) Recyclability of Au_{10} catalyst for KA oil oxidation. Reaction conditions: 1.0 mmol substrate (K/A ratio = 1/2), 2 mg catalyst, 2.1 mmol benzaldehyde, 8 mL dichloroethane, 80 °C, 1 MPa O_2 , 15 h. (e) Comparison of catalytic performances of Au_{10} and other reported catalysts for KA oil oxidation. (f) Comparison of catalytic performances of Au_{10} and other reported catalysts for cyclohexanone oxidation. Reaction parameters are shown Tables S1–S3 in the ESM.

oxidant and benzaldehyde as an assistant, both cyclohexanol (CYH) and cyclohexanone (CYC) were converted to ϵ -CL over the catalyst in high yields (77.2% and 100%, respectively), demonstrating that the Au_{10} catalyst could achieve cascade catalysis of the tandem alcohol dehydrogenation and Baeyer–Villiger oxidation. Considering the complexity of the KA oil composition obtained via cyclohexane oxidation (with a CYC/CYH ratio of approximately 0.6–0.8) [27], the scope of KA oil feedstocks with different K/A ratios in the Au_{10} -catalysed reaction was investigated comprehensively (Fig. 2(b), Fig. S1 and Table S4 in the Electronic Supplementary Material (ESM)). When the K/A ratio exceeded 1/2, 100% yields of ϵ -CL were always attained, indicating that the Au_{10} catalyst could demonstrate its broad adaptability to industrially relevant feed compositions, fully encompassing the practical K/A ratio range. Notably, the DPPF ligand and Au complexes had little activity for this reaction (Fig. 2(c)). Moreover, other atomically precise gold clusters were found to exhibit poor activity toward ϵ -CL (Fig. S2 in the ESM). This indicated that the overall structure of Au_{10} cluster (including the metal core and dual-functional peripheral ligands) played a key role in the catalytic process.

In addition, the Au_{10} clusters were highly robust under reaction conditions and could be filtered out after the reaction. Under identical conditions, the recovered catalyst remained intact and was reused in new cycles with an activity level that was almost indistinguishable from that of the fresh catalyst (Fig. 2(d) and Fig. S3 in the ESM). The ultraviolet–visible (UV–vis) spectra of other clusters just protected by a single phosphine ligand were also analyzed, clearly showing that DPPF imparted stability to the clusters through its unique chelating ability, while the $[\text{Au}_8(\text{PPh}_3)_6]^{2+}$ cluster underwent a complete decomposition during the reaction. Collectively, the Au_{10} cluster catalyst was proven sufficient to meet the need for the cascade oxidation, achieving remarkably catalytic performances for KA oil oxidation to ϵ -CL, which reached an exclusive selectivity for ϵ -CL with a yield rate of $248 \text{ mol}_{\epsilon\text{-CL}} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ (Fig. 2(d) and Table S1 in the ESM) and scale-up of the reaction gave a high turnover number (TON) of 26,390, surpassing those of representative catalytic systems under comparable conditions (Table S2 in the ESM). Additionally, in the conventional cyclohexanone oxidation reaction, the catalyst gave rise to a 100% selectivity for ϵ -CL with a yield rate of $564 \text{ mol}_{\epsilon\text{-CL}} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, much higher than other reported catalysts (Fig. 2(e) and Table S3 in the ESM).

Benzaldehyde served as a key additive for the reaction, without which no product was detected (Table S4 in the ESM), indicating that the Au_{10} cluster cannot directly catalyse the oxidation of CYC/CYH by O_2 . This agreed with literature that benzaldehyde reacts with oxygen over the catalyst to form a benzoyl hydroperoxide acid, which is the key oxygen species for subsequent oxidation of KA oil [11, 28]. To further verify this point, the O_2 and benzaldehyde were replaced by 3-chloroperbenzoic acid. The introduction of Au_{10} conferred no additional activity, confirming its primary role in the *in situ* generation of benzoyl hydroperoxide rather than downstream oxidation steps (Table S4 in the ESM). Correspondingly, the oxidation experiments of benzaldehyde and O_2 to produce benzoyl hydroperoxide showed that Au_{10} gave a benzaldehyde conversion rate of $0.18 \text{ mmol} \cdot \text{min}^{-1}$, approximately 30-fold higher than pure DPPF ligand (Fig. S4 in the ESM). This indicated that the Au_{10} catalyst facilitated the reaction of O_2 and benzaldehyde to form benzoyl hydroperoxide, which is key oxygen species for subsequent oxidation of KA oil. Therefore, the structural

origin and catalytic mechanism that enable Au_{10} to efficiently catalyse the conversion of benzaldehyde and selectively generate benzoyl hydroperoxide have become the focus of our subsequent research.

2.3 Structural evolution and active-sites formation of Au_{10}

As mentioned before, the dual-ligand (DPPF and PPh_3) structure offers Au_{10} cluster the possibility of possessing highly active open catalytic sites while maintaining structural stability. To further advance this insight, the electrospray ionization mass spectrometry (ESI-MS) was first carried out to analyze chemical formula of Au cluster. As shown in Fig. 3(a), a major peak at 2225 m/z was observed and assigned to $[\text{Au}_{10}(\text{DPPF})_4(\text{PPh}_3)_2]^{2+}$, accompanied by a small peak at 2094 m/z assigned to $[\text{Au}_{10}(\text{DPPF})_4]^{2+}$ fragment that was obtained from the removal of PPh_3 ligand during ESI-MS measurement, which suggested that the PPh_3 easily detached from the cluster. Therefore, we speculate that under the reaction conditions, the PPh_3 tends to dissociate to form highly active Au sites. According to Refs. [29–31], the active metal sites formed by such partial ligand dissociation can significantly influence the spectroscopic properties of fluorescent probe molecules. Herein, fluorescence titration with 2-naphthalenethiol (2-NT) was employed to verify this. As shown in Fig. 3(b), upon excitation at 295 nm, a $10 \text{ } \mu\text{mol} \cdot \text{L}^{-1}$ 2-NT solution exhibits significant fluorescence behavior near 350 nm, whereas an Au_{10} solution at the same concentration shows no fluorescence within this wavelength range. When equal amounts of 2-NT and Au_{10} were mixed, the characteristic fluorescence emission of 2-NT was markedly weakened to near invisibility. Increasing the concentration of 2-NT in the mixture led to a gradual increase in fluorescence intensity, but it remained consistently weaker than that of a pure 2-NT solution at the same concentration (Fig. 3(c)). Combined with the ESI-MS results, we attribute this phenomenon to the substitution of the more weakly bound PPh_3 ligands by 2-NT.

Additionally, ^{31}P nuclear magnetic resonance (NMR) spectroscopy was also conducted to investigate the coordination environment of phosphine ligands in the Au_{10} cluster. As shown in Fig. 3(d), theoretically, due to the asymmetry of the gold core, all phosphorus atoms coordinated with Au should have different chemical shifts. Therefore, multiple broad peaks were observed in the fresh Au_{10} clusters at 44–54 ppm. The multiplicity and broadening of these peaks could be attributed to the relatively slow exchange rate between different ^{31}P nuclei, which was consistent with the reported Au clusters protected by bidentate phosphine ligands [32, 33]. Notably, the Au_{10} clusters exhibited some differences after the reaction, with the broad peak positions shifting towards lower fields, indicating a decrease in P electron density within the clusters. Furthermore, the ^{31}P -NMR spectrum of Au_{10} after the reaction clearly showed a more symmetrical peak distribution, indicating a consistent chemical environment of P atoms (Au_2DPPF_2 structural unit), while the unordered spectrum of fresh Au_{10} cluster was more likely due to the superposition of two types of peaks. Combined with the results of ESI-MS and fluorescence spectra, we attribute this change to the dissociation of PPh_3 [34, 35]. These results clearly confirmed the existence of separable PPh_3 ligands offered the opportunities to form open sites on Au_{10} cluster under the premise that the rigid ligand DPPF maintained the overall structural stability of the cluster.

To investigate the effect of PPh_3 ligand dissociation on the electronic structure of the cluster theoretically, Hirshfeld atomic

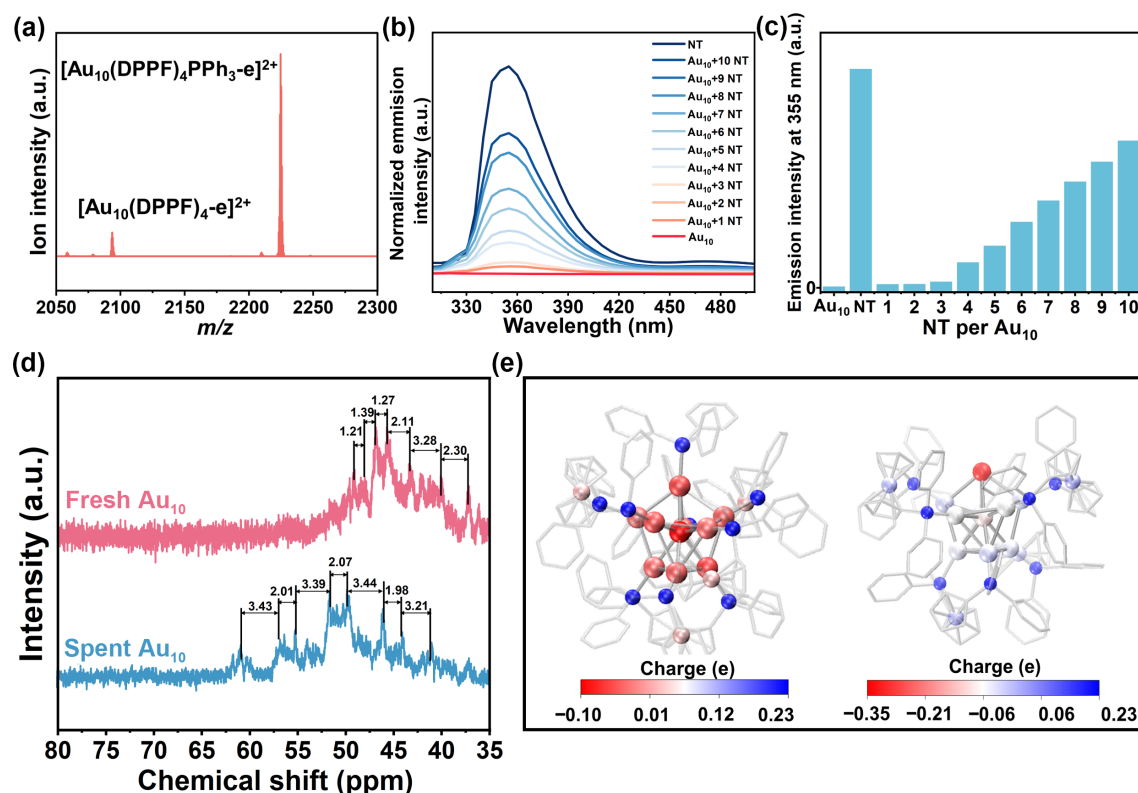


Figure 3 (a) ESI-MS data of the fresh Au_{10} cluster. (b) The emission spectra and (c) emission intensity at 355 nm of 2-NT ($10 \mu\text{mol}\cdot\text{L}^{-1}$), Au_{10} ($10 \mu\text{mol}\cdot\text{L}^{-1}$) and their mixed solutions with concentration ratios (2-NT/ Au_{10}) from 1 to 10 in $\text{MeOH}/\text{CH}_2\text{Cl}_2$ ($v/v = 1/1$). All spectra were obtained under 295 nm excitation. (d) ^{31}P NMR spectra of fresh and spent Au_{10} clusters. (e) The Hirshfeld charge distribution in Au_{10} cluster before and after PPh_3 removal.

charges were calculated using density functional theory (DFT). As shown in Fig. 3(e), the electron density in the activated state was predominantly localized on the Au_{10} core (Tables S5 and S6 in the ESM), while upon detachment of PPh_3 , the exposed Au site (that is, Au1) exhibited a markedly more negative Hirshfeld charge of -0.35 [e]. Therefore, we will next focus on investigating the role of this specific Au site (Au1 site, hereafter) and its surrounding sites in the oxidation reaction process.

2.4 Mechanism investigation

Based on the catalytic data in Section 2.2, it was believed that the key to the catalytic performance of Au_{10} lay in the high efficiency and high selectivity of the catalytic formation of benzoyl hydroperoxide species from benzaldehyde. The former was dependent on the adsorption and activation ability of O_2 and benzaldehyde while the latter relied on the stability of benzoyl hydroperoxide for reaction with CYH and CYC rather than undergoing self-quenching. Both of these aspects may depend on the unique Au sites of Au_{10} , and we began our investigation with O_2 activation. Differential charge density calculations for O_2 adsorption on Au_{10} further revealed substantial electron transfer from negatively charged Au_{10} core to the O_2 molecule, with an adsorption energy of -1.35 eV and a charge transfer of approximately $0.49 e^-$ (Fig. S5 in the ESM), suggesting that the O_2 molecule would like to be adsorbed onto the exposed Au1 site (note: herein and throughout all subsequent calculations, the phenyl groups of the DPPF ligand were replaced with methyl groups to reduce computational cost). This intense electron transfer likely promotes O_2 activation to form reactive oxygen species. Therefore, we added 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a radical trap to

coexisting system of Au_{10} and O_2 and collected its electron paramagnetic resonance (EPR) spectrum. For the Au_{10} system (Fig. 4(a)), the characteristic EPR signals of superoxide radical ($\text{DMPO} \cdot \text{O}_2^-$) were detected, while pure DPPF obviously failed to complete the conversion [36]. Besides, quenching experiments further confirmed that the oxidation proceeded via a radical-mediated pathway, in which the introduction of 1,4-benzoquinone as an O_2^- scavenger led to a significant inhibition of catalytic activity, implying that superoxide radicals play a decisive role in the reaction process (Fig. S6 in the ESM). Furthermore, the adsorption behavior of benzaldehyde over the Au_{10} catalyst was studied by Fourier transform infrared spectroscopy (FTIR). In Fig. 4(b), when benzaldehyde was adsorbed onto the Au_{10} catalyst at room temperature, the bands at 1697 , 1597 , and 1583 cm^{-1} , respectively assigned to the stretching vibrations of the carbonyl group and benzene skeleton were found [37]. After removing physisorbed species, the two vibration bands of benzene skeleton became weak while the carbonyl group band shifted to 1684 cm^{-1} , which was speculatively attributed to the benzaldehyde adsorbed on the Au_{10} cluster via the carbonyl group. In contrast to benzaldehyde, the IR bands from cyclohexanol and cyclohexanone adsorbed onto the catalyst disappeared completely after purging, indicating that Au_{10} preferentially adsorbed benzaldehyde (Fig. S7 in the ESM).

Combined with the rapid oxidation of benzaldehyde with the catalysis of Au_{10} mentioned in Fig. S4 in the ESM, the efficient generation of O_2^- species and the effective adsorption of benzaldehyde could be regarded as the fundamental reasons for the high activity of the Au_{10} catalyst. However, the generated peroxyacid species and their role in the cascade oxidation process still require further experimental confirmation.

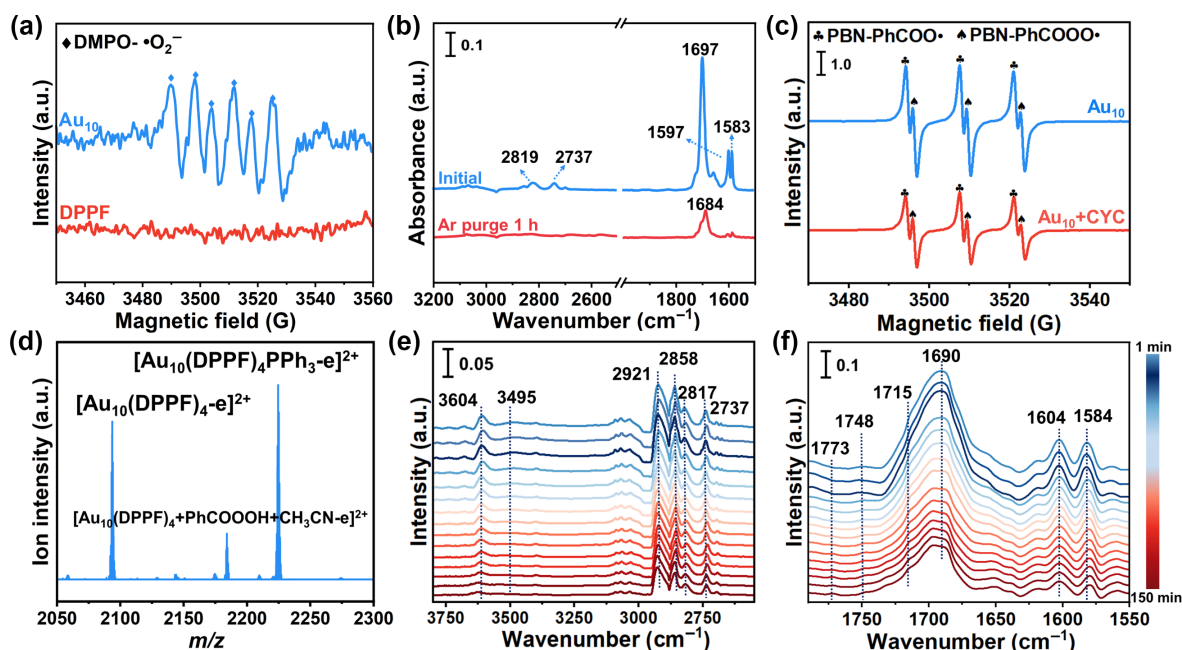


Figure 4 (a) EPR spectra with DMPO as a trap obtained from Au₁₀ system and DPPF system, respectively. (b) *In situ* FTIR spectra of adsorbed benzaldehyde on Au₁₀. (c) EPR spectra with PBN as radical trap from the Au₁₀ catalyst systems before and after adding cyclohexanone. (d) ESI-MS data of captured cluster during the reaction. (e) and (f) Time-resolved *in situ* FTIR spectra obtained from the KA oil oxidation on the Au₁₀ catalyst.

Therefore, *in situ* EPR measurements using N-tert-butyl-α-phenylnitron (PBN) as a spin trapping agent revealed two types of free radical signals during Au₁₀-catalyzed benzaldehyde oxidation (Fig. 4(c)). The two triplets were assigned to [PBN-PhCOO·] and [PhCOOO·] radical adducts, respectively [38, 39] suggesting that Au₁₀ catalyst enabled the benzaldehyde oxidation into benzoylperoxy radicals [PhCOOO·]. Under reaction conditions, the EPR signal was significantly weakened upon the introduction of cyclohexanone, further supporting that benzoyl hydroperoxide was indeed crucial oxygen species for KA oil oxidation. More notably, ESI-MS was performed to capture the Au₁₀ cluster intermediates during the reaction (Fig. 4(d)). The cluster lost PPh₃ ligand under reaction conditions and especially a distinct mass peak at 2185 *m/z* assigned to [Au₁₀(DPPF)₄+PhCOOOH+CH₃CN-e]²⁺ was trapped (note that CH₃CN was from the ESI-MS measurement rather than from the reaction system), showing that PhCOOOH was generated on the activated Au₁₀ cluster during the reaction.

Time-resolved *in situ* FTIR spectroscopy was carried out to detect the reaction intermediates. As shown in Figs. 4(e) and 4(f), the bands at 3604 and 3495 cm⁻¹, assigned to the ν(-OH) stretching vibrations of cyclohexanol, gradually diminished as the reaction progressed, indicating the continuous consumption of cyclohexanol. Simultaneously, the intensity of the bands at 1690 and 1584/1604 cm⁻¹, corresponding to the ν(C=O) and ν(C=C) vibrations of benzaldehyde, respectively, decreased with reaction time. In contrast, two new bands emerged in 1773 and 1748 cm⁻¹ assigned to the carbonyl stretching vibrations of benzoyl hydroperoxide and ε-CL, respectively, and intensified progressively. The band at 1715 cm⁻¹ attributed to the ν(C=O) vibration of cyclohexanone showed a slight increase in the early stage of the reaction, which was then gradually consumed. Taken together, the IR results revealed that benzoyl hydroperoxide was efficiently generated on the Au₁₀ catalyst and subsequently reacted with cyclohexanol to form cyclohexanone, and was finally converted to ε-CL [40].

Furthermore, we performed detailed DFT calculations on the catalytic cascade oxidation process based on the precise structure of Au₁₀ cluster. As displayed in Fig 5(a), the reaction was initiated by dissociation of the PPh₃ ligand, yielding Int 1 (Fig. 4(d)) that was employed as the starting point of calculations. The dissociation of this ligand enabled the generation of an unsaturated Au1 site. Subsequently, O₂ was activated at the unsaturated Au1 site, leading to the formation of Int 2. PhCHO then inserts into the gap between the Au1 and Au2 sites, yielding Int 3. In this configuration, the carbonyl hydrogen was close to Au2, and the adsorption facilitated a charge transfer of -0.20 e from the Au₁₀ cluster to PhCHO, stabilizing the system by 1.11 eV. C-H bond cleavage then proceeded via TS-1 (energy barrier: 1.29 eV), generating Int 4 where PhCO bridges the two Au sites (Au1 and Au2) and H adsorbs on Au2. Subsequently, C-O bond formation between the carbonyl carbon of PhCO and a terminal oxygen of the activated O₂ occurred via TS-2 (energy barrier: 0.86 eV), generating Int 5, in which a PhCOOO group was bound to the Au1 site. The H atom originally bound to Au2 site then transferred to the bridging site between Au1 and Au2 (Int 6), and finally transferred via TS-3 (energy barrier: 0.55 eV) to form the Int 7, where a PhCOOOH molecule was weakly adsorbed on the Au₁₀ cluster. Upon desorption of PhCOOOH and subsequent structural relaxation, the cluster returned to Int 1, completing the catalytic cycle.

During this process, the Au2 site was not a spectator but deeply involved in the adsorption of substrates and intermediates. The dynamic change in its spatial configuration relative to the Au1 site has drawn our attention. To illustrate this more clearly, Figs. 5(b) and 5(c) show the proximity of the two active gold atoms marked as Au1 and Au2 along the reaction with sequent eight events from I to VIII. While the weakly bound PPh₃ only coordinates with the apical Au1 atom and was easily dissociated (event I), thereby generating accessible unsaturated Au1 active site and meanwhile the Au1-Au2 bond broke (4.21 Å for the distance between Au1 and Au2), which provided chances to activate dioxygen and

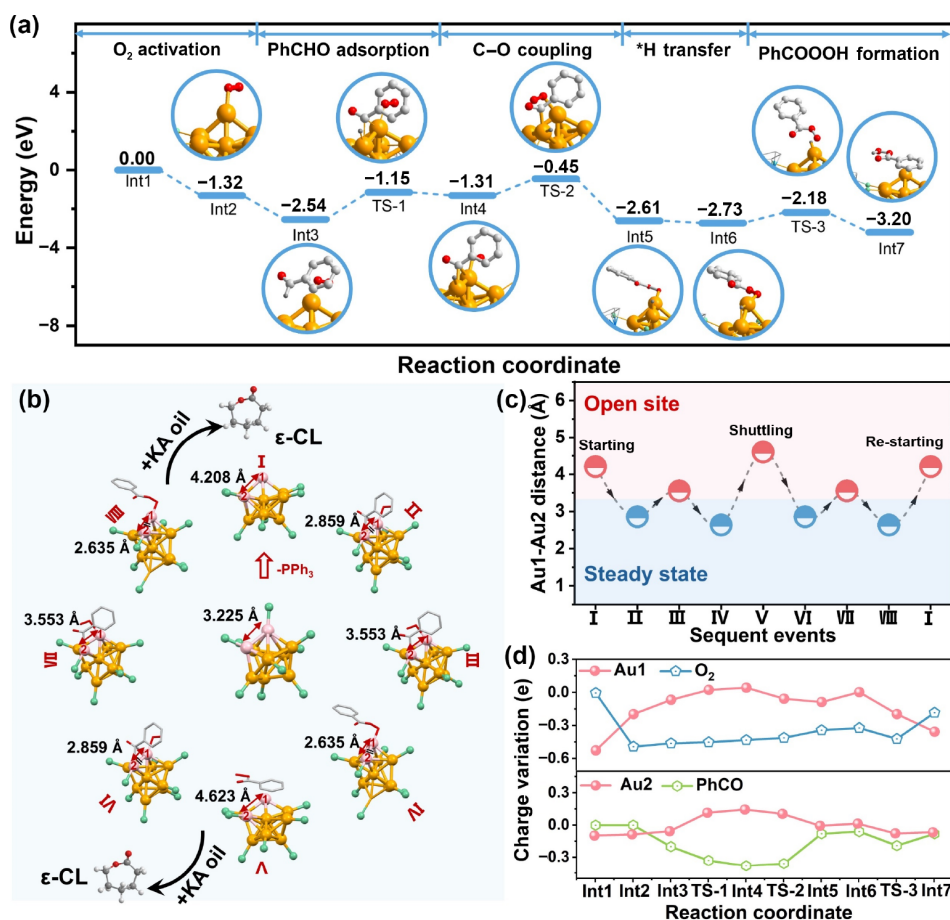


Figure 5 (a) The DFT energy profiles and corresponding local structures of cluster and key intermediates along the reaction pathway. Color code: Au = orange, C = grey, O = red, Fe = blue, P = green, H = dark grey. (b) Schematic mechanism of rhymical response of Au₁₀(DPPF)₄PPh₃ to KA oil oxidation. The two active atoms are marked Au1 and Au2. (c) The distance change of the two active Au atoms during the eight events from I to VIII. (d) Charge variation of Au1, Au2, adsorbed O₂ and adsorbed PhCO along the reaction pathway.

benzaldehyde (event II). The benzaldehyde was bridged over the two Au atoms, leading to the interlinkage of Au1 and Au2 again (a distance of 2.86 Å). The active oxygen attacked the adsorbed benzaldehyde, making the bridged mode transfer into the linear mode on the Au2 site (event III), and in this way the Au2 kept away from Au1 (a distance of 3.55 Å). Subsequently, the formation of benzoyl hydroperoxide intermediate in the Au1 resulted in the structural rearrangement of Au₁₀ (event IV) and the close communication between Au1 and Au2 (a distance of 2.64 Å). The hydroperoxide intermediate desorbed from the Au1 and then oxidized the KA oil to produce ε-CL (event V), which further convinced the Au1 and Au2 of the farewell (a distance of 4.62 Å) for being active sites in next shuttling (from event VI to event VIII). This mechanism ensured a continuous and sufficient supply of PhCOOOH for subsequent reactions. It bears emphasizing that, during the reaction, the subtle rearrangement of Au sites within the Au₁₀ cluster is expected to occur seamlessly, without the need for a large energy input to initiate dynamic reconstruction and establish controllable spatial proximity between active sites, as is required for other catalysts [41].

In addition, we tracked the evolution of Hirshfeld charges along the reaction coordinate. As shown in Fig. 5(d), both Au1 and Au2 sites exhibited increasing positive charge during the process, reflecting electron flow into O₂ and PhCO, thereby highlighting the electron-rich character of the Au₁₀ core and its role in activating

small molecules via electron donation. The result was in good agreement with the adsorption behavior of benzaldehyde on the Au₁₀ cluster, that the carbonyl group red shifted to 1684 cm⁻¹, which was speculatively attributed to the decreased bond force constant of C=O.

We further discussed the oxidation of CYH and CYC using PhCOOO⁻ species as the oxidant: (1) As shown in Fig. S9 in the ESM, CYH underwent protonation under acidic conditions to form the cyclohexanol oxonium ion (Int 8), which dehydrated to give the cyclohexyl carbocation (Int 9) with an energy increase of 1.35 eV. This carbocation was then attacked by the terminal oxygen of the PhCOOO⁻, affording Int 10. Subsequent transformation proceeded through a six-membered cyclic transition state TS-4, which involved concerted proton transfer and O-O bond rupture (energy barrier: 0.72 eV), yielding CYC and PhCOOH. (2) As illustrated in Fig. S10 in the ESM, the carbonyl carbon of protonated CYC (Int 11) underwent nucleophilic attack by the terminal oxygen of peroxybenzoate to form Int 12. The latter rearranged via oxygen migration through TS-5 (energy barrier: 0.85 eV) to give Int 13, followed by a proton-transfer step via a six-membered cyclic TS-6 (energy barrier: 0.16 eV) leading Int 14, a complex of PhCOOH and ε-CL. Dissociation of Int 14 released free ε-CL resulting in an energy rising of 1.06 eV. The oxidation of CYH and CYC were exothermic by -4.89 and -4.84 eV, respectively. Overall, the calculations unambiguously supported the responsiveness of local sites on Au₁₀ cluster to reactive species in the catalytic cycle.

3 Conclusion

In summary, we report a customized catalysis of the $\text{Au}_{10}(\text{DPPF})_4\text{PPh}_3$ cluster for KA oil oxidation to ϵ -CL in one-pot synthesis on the single catalyst. The dual-ligand protected structure promotes the formation of highly active open catalytic sites in the Au_{10} cluster while maintaining structural stability, enabling the conversion of O_2 to O_2^- species and effective adsorption of benzaldehyde. The further study reveals a rhythmical catalytic response of Au_{10} cluster to the oxidation of KA oil, achieving a high efficiency for ϵ -CL production. The apical Au atom of the cluster is exposed and adjacent Au–Au bond is opened to become active sites, when the PPh_3 ligand departs from the cluster. Sequentially, the two active Au atoms struggle to approach for absorbing benzaldehyde, after that they keep away from each other to abandon benzoyl hydroperoxide from the reaction of benzaldehyde and dioxygen. This structural sensitivity of the cluster during catalysis enables continuous generation of benzoyl hydroperoxide to oxidize KA oil while preserving the structural integrity of the cluster. These clusters hold promise in decoupling the interactive communication between active sites and reactive species, which deserves more future efforts to unravel the nature of catalysis.

4 Experimental

All materials and methods can be found in the ESM.

Electronic Supplementary Material: Supplementary material (catalytic performance; UV–vis spectra; differential charge density calculation; radical scavenger experiments; the detailed *in situ* FTIR spectra; the pathway and detailed optimized structures in the DFT calculation; the Hirshfeld charge distribution) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908863>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

We acknowledge financial support from the National Natural Science Foundation of China (Nos. 22125202, 92461312, and U24A20487) and SINOPEC Research Institute of Petroleum Processing Co., Ltd.

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. Z. designed research. X. Y. X. performed research. Y. N. Z. and S. H. L. performed calculations. Y. Q. T., H. W., G. D. W., and Q. Y. contributed analytic tools. All authors wrote the paper.

Use of AI statement

None.

References

- [1] Labet, M.; Thielemans, W. Synthesis of polycaprolactone: A review. *Chem. Soc. Rev.* **2009**, *38*, 3484–3504.
- [2] Woodruff, M. A.; Huttmacher, D. W. The return of a forgotten polymer-polycaprolactone in the 21st century. *Prog. Polym. Sci.* **2010**, *35*, 1217–1256.
- [3] Wei, X. W.; Gong, C. Y.; Gou, M. L.; Fu, S. Z.; Guo, Q. F.; Shi, S.; Luo, F.; Guo, G.; Qiu, L. Y.; Qian, Z. Y. Biodegradable poly(ϵ -caprolactone)-poly(ethylene glycol) copolymers as drug delivery system. *Int. J. Pharmaceut.* **2009**, *381*, 1–18.
- [4] González-Martínez, D.; Rodríguez-Mata, M.; Méndez-Sánchez, D.; Gotor, V.; Gotor-Fernández, V. Lactonization reactions through hydrolase-catalyzed peracid formation. Use of lipases for chemoenzymatic Baeyer–Villiger oxidations of cyclobutanones. *J. Mol. Catal. B: Enzym.* **2015**, *114*, 31–36.
- [5] Zhang, Y. Y.; Zhao, Y. Y.; Jiang, W. W.; Yao, Q. C.; Li, Z. W.; Gao, X.; Liu, T.; Yang, F. K.; Wang, F. Y.; Liu, J. H. Lipase-catalyzed oxidation of cyclohexanone to form ϵ -caprolactone and kinetic modeling. *ACS Sustain. Chem. Eng.* **2019**, *7*, 13294–13306.
- [6] Rios, M. Y.; Salazar, E.; Olivo, H. F. Baeyer–Villiger oxidation of substituted cyclohexanones via lipase-mediated perhydrolysis utilizing urea-hydrogen peroxide in ethyl acetate. *Green Chem.* **2007**, *9*, 459–462.
- [7] Zhou, W. J.; Wischert, R.; Xue, K.; Zheng, Y. T.; Albela, B.; Bonneviot, L.; Clacens, J. M.; De Campo, F.; Pera-Titus, M.; Wu, P. Highly selective liquid-phase oxidation of cyclohexane to KA oil over Ti-MWW catalyst: Evidence of formation of oxyl radicals. *ACS Catal.* **2014**, *4*, 53–62.
- [8] Yuan, H. X.; Xia, Q. H.; Zhan, H. J.; Lu, X. H.; Su, K. X. Catalytic oxidation of cyclohexane to cyclohexanone and cyclohexanol by oxygen in a solvent-free system over metal-containing ZSM-5 catalysts. *Appl. Catal. A: Gen.* **2006**, *304*, 178–184.
- [9] Fukuda, O.; Sakaguchi, S.; Ishii, Y. A new strategy for catalytic Baeyer–Villiger oxidation of KA-oil with molecular oxygen using N-hydroxyphthalimide. *Tetrahedron Lett.* **2001**, *42*, 3479–3481.
- [10] Schmidt, S.; Scherkus, C.; Muschiol, J.; Menyes, U.; Winkler, T.; Hummel, W.; Gröger, H.; Liese, A.; Herz, H. G.; Bornscheuer, U. T. An enzyme cascade synthesis of ϵ -caprolactone and its oligomers. *Angew. Chem., Int. Ed.* **2015**, *54*, 2784–2787.
- [11] Xue, G. X.; Liu, H. L.; Liu, W.; Yang, C. Y.; Ban, Z. Y.; An, P. F.; Chen, W. X.; Zheng, L. R.; Li, G. D.; Tan, T. et al. Major-auxiliary cooperative metal pairs in MOFs enable cascade oxidation of KA oil to ϵ -caprolactone. *Nat. Commun.* **2024**, *15*, 9659.
- [12] Yang, X. F.; Wang, A. Q.; Qiao, B. T.; Li, J.; Liu, J. Y.; Zhang, T. Single-atom catalysts: A new frontier in heterogeneous catalysis. *Acc. Chem. Res.* **2013**, *46*, 1740–1748.
- [13] Védreine, J. C. Revisiting active sites in heterogeneous catalysis: Their structure and their dynamic behaviour. *Appl. Catal. A: Gen.* **2014**, *474*, 40–50.
- [14] Vogt, C.; Weckhuysen, B. M. The concept of active site in heterogeneous catalysis. *Nat. Rev. Chem.* **2022**, *6*, 89–111.
- [15] Wang, D. G.; Wu, J. X.; Jiao, L. Y.; Xie, L. M. *In situ* identification of active sites during electrocatalytic hydrogen evolution. *Nano Res.* **2023**, *16*, 12910–12918.
- [16] Shi, Y. J.; Zhou, Y. W.; Lou, Y.; Chen, Z. P.; Xiong, H. F.; Zhu, Y. F. Homogeneity of supported single-atom active sites boosting the selective catalytic transformations. *Adv. Sci.* **2022**, *9*, 2201520.
- [17] Cui, X. J.; Li, W.; Ryabchuk, P.; Junge, K.; Beller, M. Bridging homogeneous and heterogeneous catalysis by heterogeneous single-metal-site catalysts. *Nat. Catal.* **2018**, *1*, 385–397.
- [18] Cai, X.; Hu, W. G.; Xu, S.; Yang, D.; Chen, M. Y.; Shu, M.; Si, R.; Ding, W. P.; Zhu, Y. Structural relaxation enabled by internal vacancy available in a 24-atom gold cluster reinforces catalytic reactivity. *J. Am. Chem. Soc.* **2020**, *142*, 4141–4153.
- [19] Cai, X.; Saranya, G.; Shen, K. Q.; Chen, M. Y.; Si, R.; Ding, W. P.;

- Zhu, Y. Reversible switching of catalytic activity by shuttling an atom into and out of gold nanoclusters. *Angew. Chem., Int. Ed.* **2019**, *58*, 9964–9968.
- [20] Liu, Y. Y.; Chai, X. Q.; Cai, X.; Chen, M. Y.; Jin, R. C.; Ding, W. P.; Zhu, Y. Central doping of a foreign atom into the silver cluster for catalytic conversion of CO₂ toward C–C bond formation. *Angew. Chem., Int. Ed.* **2018**, *57*, 9775–9779.
- [21] Li, G. J.; Sui, X.; Cai, X.; Hu, W. G.; Liu, X.; Chen, M. Y.; Zhu, Y. Precisely constructed silver active sites in gold nanoclusters for chemical fixation of CO₂. *Angew. Chem., Int. Ed.* **2021**, *60*, 10573–10576.
- [22] Koshland, D. E. Jr. The key-lock theory and the induced fit theory. *Angew. Chem., Int. Ed.* **1995**, *33*, 2375–2378.
- [23] Regalbuto, J. R.; Datye, A. K. All the lonely atoms, where do they all belong. *Nat. Nanotechnol.* **2022**, *17*, 110–111.
- [24] Li, G. J.; Li, G. A.; Liang, X. Y.; Tian, Y. Q.; Lu, J. Z.; Xu, X. Y.; Liu, X.; Ma, J.; Li, S. H.; Zhu, Y. An atomically precise Au₁₀(DPPF)₄PPh₃ cluster catalyst for N-hydroformylation of amines. *Chem. Sci.* **2025**, *16*, 18642–18651.
- [25] Dong, Y. Y.; Liu, C. Y.; Shi, W. Q.; Guan, Z. J.; Wang, Q. M. A stable open-shelled Au₂₆ nanocluster with remarkable performance in selective oxidation of benzyl alcohol. *Angew. Chem., Int. Ed.* **2025**, *64*, e202420314.
- [26] Yuan, S. F.; Lei, Z.; Guan, Z. J.; Wang, Q. M. Atomically precise preorganization of open metal sites on gold nanoclusters with high catalytic performance. *Angew. Chem., Int. Ed.* **2021**, *60*, 5225–5229.
- [27] Vomeri, A.; Stucchi, M.; Villa, A.; Evangelisti, C.; Beck, A.; Prati, L. New insights for the catalytic oxidation of cyclohexane to K-A oil. *J. Energy Chem.* **2022**, *70*, 45–51.
- [28] ten Brink, G. J.; Arends, I. W. C. E.; Sheldon, R. A. The Baeyer-Villiger reaction: New developments toward greener procedures. *Chem. Rev.* **2004**, *104*, 4105–4124.
- [29] de Silva, N.; Ha, J. M.; Solovyov, A.; Nigra, M. M.; Ogino, I.; Yeh, S. W.; Durkin, K. A.; Katz, A. A bioinspired approach for controlling accessibility in calix[4]arene-bound metal cluster catalysts. *Nat. Chem.* **2010**, *2*, 1062–1068.
- [30] Ha, J. M.; Solovyov, A.; Katz, A. Synthesis and characterization of accessible metal surfaces in calixarene-bound gold nanoparticles. *Langmuir* **2009**, *25*, 10548–10553.
- [31] Sufyan, S. A.; van Devenner, B.; Nigra, M. M. Synthesis of highly accessible and reactive sites in gold nanoparticles using bound bis(Diphenylphosphine) ligands. *Chem.—Eur. J.* **2022**, *28*, e202202877.
- [32] Zhang, Q. F.; Williard, P. G.; Wang, L. S. Polymorphism of phosphine-protected gold nanoclusters: Synthesis and characterization of a new 22-gold-atom cluster. *Small* **2016**, *12*, 2518–2525.
- [33] McKenzie, L. C.; Zaikova, T. O.; Hutchison, J. E. Structurally similar triphenylphosphine-stabilized undecagolds, Au₁₁(PPh₃)₇Cl₃ and [Au₁₁(PPh₃)₈Cl₂]Cl, exhibit distinct ligand exchange pathways with glutathione. *J. Am. Chem. Soc.* **2014**, *136*, 13426–13435.
- [34] Nguyen, T. A.; Penouilh, M. J.; Cattey, H.; Pirio, N.; Fleurat-Lessard, P.; Hierso, J. C.; Roger, J. Unsymmetrically substituted bis(phosphino)ferrocenes triggering through-space ³¹(P, P′)-nuclear spin couplings and encapsulating coinage metal cations. *Organometallics* **2021**, *40*, 3571–3584.
- [35] Ciabatti, I.; Femoni, C.; Iapalucci, M. C.; Longoni, G.; Lovato, T.; Zacchini, S. PPh₃-derivatives of [Pt_{3n}(CO)_{6n}]^{2−} (n = 2–6) Chini's clusters: Syntheses, structures, and ³¹P NMR Studies. *Inorg. Chem.* **2013**, *52*, 4384–4395.
- [36] Reszka, K.; Bilski, P.; Chignell, C. F. EPR spectra of DMPO spin adducts of superoxide and hydroxyl radicals in pyridine. *Free Radic. Res. Commun.* **1992**, *17*, 377–385.
- [37] Yu, J.; Zhang, P.; Li, L. L.; Li, K. L.; Zhang, G.; Liu, J.; Wang, T.; Zhao, Z. J.; Gong, J. L. Electroreductive coupling of benzaldehyde by balancing the formation and dimerization of the ketyl intermediate. *Nat. Commun.* **2022**, *13*, 7909.
- [38] Sankar, M.; Nowicka, E.; Carter, E.; Murphy, D. M.; Knight, D. W.; Bethell, D.; Hutchings, G. J. The benzaldehyde oxidation paradox explained by the interception of peroxy radical by benzyl alcohol. *Nat. Commun.* **2014**, *5*, 3332.
- [39] Tang, J. T.; Jiang, Z. W.; Gao, Z.; Xie, Q. J.; Gu, S.; Chen, A. Q.; Yuan, J. Y.; Li, W.; Tang, R. R.; Yu, G. P. Hydroxyl radical mediated heterogeneous photocatalytic Baeyer–Villiger oxidation over covalent triazine/heptazine-based frameworks. *Angew. Chem., Int. Ed.* **2025**, *64*, e202416879.
- [40] Fu, C. H.; Chen, G. Y.; Lin, Y. H.; Lin, C. H.; Muthiah, B.; Kasai, T.; Morita, K.; Mito, H.; Espulgar, W.; Santos, G. N. et al. Kinetic and equilibrium analysis of peracetic acid formation at 1753 cm^{−1} mid-infrared absorption peak using facile attenuated total reflection Fourier transform infrared technique. *J. Chin. Chem. Soc.* **2023**, *70*, 1427–1434.
- [41] Hai, X.; Zheng, Y.; Yu, Q.; Guo, N.; Xi, S. B.; Zhao, X. X.; Mitchell, S.; Luo, X. H.; Tulus, V.; Wang, M. et al. Geminal-atom catalysis for cross-coupling. *Nature* **2023**, *622*, 754–760.

