Pt$_1$ enhanced C-H activation synergistic with Pt$_n$ catalysis for glycerol cascade oxidation to glyceric acid

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The selective oxidation of glycerol to glyceric acid, an important value-added reaction from polyols, is a typical cascade catalytic process. It is still of great challenge to simultaneously achieve high glycerol activity and glyceric acid selectivity, suffering from either deep oxidation and C-C cleavage or poor oxidation efficiency from glyceraldehyde to glyceric acid. Herein, this work, inspired by nature, proposes a cascade synergistic catalysis strategy by atomic and low-coordinated cluster Pt on well-defined Cu-CuZrO$_x$, which involves enhanced C-H activation on atomic Pt$_1$ and O-H activation on cluster Pt$_n$ in the oxidation of glycerol to glyceraldehyde, and cluster Pt$_n$ for C=O activation followed by O-H insertion and atomic Pt$_1$ for C-H activation in the tandem oxidation of glyceraldehyde to glyceric acid. The enhanced C-H activation in the cascade process by atomic Pt$_1$ is revealed to be essential for the high glycerol activity (90.0±0.1%) and the glyceric acid selectivity (80.2±0.2%).

Effective construction of chemical bonds and/or efficient synthesis of functional compounds usually requires multiple elementary steps or even cascade reactions$^{1-3}$. Natural biological systems effectively produce elaborate molecules in the form of cascade reactions by multiple biocatalysts$^{4,5}$. Inspired by nature, catalytic cascade reaction in chemical synthesis has been developed to enable multistep transformation in a one-pot manner, thereby circumventing the isolation of unstable or toxic intermediates and improving the atom economy and overall yields$^{6,7}$. In cascade catalysis, the reactivity and selectivity could additionally be enhanced by evading equilibrium reactions by the cooperative effects of multiple catalysts or multiple catalytic active sites$^{8-10}$. But how to achieve satisfactory cascade catalysis remains challenging in terms of selectivity. The reaction tends to stay in the intermediate without subsequent conversion since the cascade steps are hard to be coupled in a precise and smooth relay manner. This work proposes a strategy on cascade synergistic catalysis for the efficient selective oxidation of glycerol to glyceric acid (GLYA) as a showcase, which is a typical cascade oxidation process and has been a longtime key problem towards the selective oxidation of C-O bonds in the biomass value-added processes.

Glycerol is an abundant side-product in the production of biodiesel via transesterification, which has been of major concern$^{8,9}$. The selective oxidation of glycerol to GLYA, which possesses physiological activity and is used directly or as intermediates in the fields of drug and pharmaceutical manufacture, is an important value-added reaction from polyols$^{10-13}$. With the rising global concerns about energy and the environment, the exploitation of biomass as clean and renewable energy provides one promising strategy to conform the demand of escalating energy$^{14-15}$. The efficient conversion of glycerol to value-added fine chemicals is quite demanded more than ever$^{16-20}$. The cascade catalytic process includes the dehydrogenation of primary O-H and C-H bonds of glycerol to glyceraldehyde (GLAD) as intermediate, and the subsequent C=O activation of GLAD followed by the O-H insertion and the additional dehydrogenation to GLYA$^{21-23}$. The problem of low GLYA selectivity, the common challenge in cascade catalysis, is one of the main challenges due to the powerless transformation from GLAD to GLYA, and/or the deep oxidation and C-C

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Despite that alloying Pt with a second metal component has been proposed not only to promote the oxidation of GLAD to GLYA (Step II). Superior to the sole cluster/motivated by the literature survey on Pt/Cu single-atom alloy in demonstrating the cascade synergistic catalysis strategy. Our rationale is GLAD followed by enhanced C-H activation on atomic Pt in the tan-based bimetallic alloy (i.e., Au27 signifying activation by atomic Pt synergistic with low-coordinated Pt-Pt for the obtaining a moderate GLYA yield.

Herein, a cascade synergistic catalysis strategy on enhanced C-H activation by atomic Pt synergic with low-coordinated Pt-Pt for the cascade selective oxidation of glycerol to GLYA has been demonstrated. Supported multiple PtCu active sites, integrating atomic Pt and cluster Pt on well-defined Cu-CuZrOx, have been developed to demonstrate the cascade synergistic catalysis strategy. Our rationale is motivated by the literature survey on Pt/Cu single-atom alloy in catalytic dehydrogenation, in which the isolated Pt atoms with unique electron-rich characters could facilitate the activation of the C-H bonds with intermediate barriers. In this work (Fig. 1), the proposed cascade synergistic catalysis includes: (1) the enhanced C-H activation on atomic Pt and O-H activation on cluster Pt in the oxidation of glycerol to 2-adsorbed GLAD (Step I); (2) the O-H insertion of 2-adsorbed GLAD followed by enhanced C-H activation on atomic Pt in the tandem oxidation of GLAD to GLYA (Step II). Superior to the sole cluster/ nanoparticles PtM catalysis, the enhanced C-H activation by the atomic Pt in the cascade synergy has been proposed not only to promote the glycerol conversion to GLAD, but to enhance the transformation of GLAD to GLYA in high selectivity to avoid deep oxidation and C-C cleavage, accordingly achieving both high glycerol conversion and high GLYA selectivity.

Results
Atomic and cluster Pt sites on Cu-CuZrOx
To be specific, the introduction of atomic Pt and cluster Pt sites was achieved by a galvanic replacement reaction on the surface of Cu nanoparticles (Supplementary Fig. 1a), which were prepared by in situ dissolution from the zirconium/copper mixed oxide. According to the ratio of zirconium and copper of 4.3:1 from ICP characterization, the precursor is denoted as CuZr4.3O9.6. As shown in the XRD pattern (Supplementary Fig. 1b), CuZr4.3O9.6 was identified as CuZrO3 phase in orthorhombic shape (JCPDS 43-0953) with no other impurities. The morphology is an agglomerated flakes type with a rough surface (Supplementary Fig. 2a). In the H2-TPR (Supplementary Fig. 2b), two observed H2 consumptions at 176 and 233 °C could be attributed to the reduction of Cu-O-Cu and Cu-O-Zr species, respectively. The reduction was carried out under 450 °C with a H2 stream to obtain supported Cu nanoparticles with a partial Cu reduction from bulk CuZr4.3O9.6 (Cu-CuZrOx), according to the Cu 2p core-level X-ray photoelectron spectroscopy (XPS) spectra (Supplementary Fig. 3a). As shown in the HRTEM images (Supplementary Fig. 4a), Cu nanoparticles with a maximum size distribution of around 3.4 nm are well-dispersed on the agglomerated oxide flakes in particle size of 50–100 nm. The Cu (111) plane (lattice spacing: 0.209 nm) is resolved (Supplementary Fig. 4b), consistent with the appearance of a tiny reflection of the Cu (111) in the XRD pattern (Supplementary Fig. 1b).

Afterward, a galvanic replacement method was employed to introduce Pt atoms onto the Cu surface with a Pt loading of 0.3 and 0.9 wt% (Supplementary Table 1). It is noted from XRD patterns that the Pt replacement made no significant changes in the crystalline structure without resolved Pt phase (Supplementary Fig. 1b), implying a high dispersion degree of Pt species. In a Pt loading of 0.5 wt% (Fig. 2a), the nanoparticles in a Cu (111) plane show a maximum size distribution of around 3.3 nm on the oxide flakes close to Cu-CuZrO3 (Supplementary Fig. 4a). In the aberration-corrected high-angle annular dark field scanning transmission electron microscopy (AC-HAADF-STEM) image (Fig. 2b), single Pt atoms (red circle) are located on Cu (111) planes and no Pt atoms are resolved on the oxide. The STEM-coupled energy dispersive spectroscopy (EDS) element mapping (Fig. 2c) of Pt (blue), Cu (yellow), Zr (olive), and O (red) presents a uniform and high dispersion of Pt sites on the Cu nanoparticles, confirming the atomically-dispersed Pt site (0.5%PtCu-CuZrOx). With an increased Pt loading of 0.9%, no visible Pt nanoparticles are resolved instead of Cu (111) nanoparticles (~3.4 nm) (Fig. 2d). Demonstrated by AC-HAADF-STEM images (Fig. 2e), a few Pt clusters around 1.2 nm (olive circle) coexist nearby the atomic Pt (red circle) (0.9%PtCu-CuZrOx). The 3D surface simulation of the marked regions (yellow rectangles) verifies the adjacent spatial distribution of atomic Pt and cluster Pt in the XRD pattern (Supplementary Fig. 5). In the brightness intensity profiles (Supplementary Fig. 6), a distance between atomic Pt and the Pt cluster for the two marked line I and II is determined to be ~0.18 and ~0.22 nm, further confirming the adjacent spatial distribution. Considering the bond length (1.439 Å) of the primary C-O in glycerol, it provides the...
possibility to form synergistic adsorption of the primary C-O on the adjacent atomic Pt₁ and cluster Ptₙ sites as expected. The STEM-EDS mappings (Fig. 2f) confirm the coexistence of atomic Pt and cluster Pt sites. Additional HRTEM and AC-HAADF-STEM images are provided in Supplementary Fig. 7.

In the Fourier-transformed extended X-ray absorption fine structure spectra (FT-EXAFS, Fig. 2g) at the Pt L₃-edge, 0.5%Pt₁/Cu-CuZrOₓ exhibits one dominant peak in the region around 2.3 Å located between PtO₂ and Pt foil, demonstrating the formation of Pt-Cu coordination according to the references. As fitted (Supplementary Table 2), only 8.3 Pt-Cu coordination was identified without any Pt-Pt or Pt-O coordination detected. Whereas, 0.9%Pt₁ + Ptₙ/Cu-CuZrOₓ presents a much broader peak in the region around 2.3 Å with an asymmetric shoulder peak in the region around 2.3 Å corresponding to Pt-Cu and Pt-Pt coordination structure with fitted 6.1 Pt-Cu and 3.0 Pt-Pt coordination, confirming the coexistence of atomic Pt₁ and cluster Ptₙ. In situ CO-absorbed diffuse reflectance infrared Fourier transform spectroscopy measurements (CO-DRIFTS, Fig. 2h) were performed to probe the atomic geometry configuration of Pt sites on the Cu surface. On Cu-CuZrOₓ as control, a weak and broad absorption band at 2099 cm⁻¹ associated with chemisorbed CO on Cu⁰ species appears. On 0.5%Pt₁/Cu-CuZrOₓ, two deconvoluted bands by multi-peaks Gaussian fitting are observed at 2105 and 2062 cm⁻¹, respectively. By comparison to Cu-CuZrOₓ, the former band is attributed to the chemisorbed CO absorption on Cu⁰ species in an electron-deficient state due to the Cu-Pt coordination. The latter is associated with the linearly-bonded CO on atomic Pt. On 0.9% Pt₁ + Ptₙ/Cu-CuZrOₓ, besides the bands for CO adsorbed on Cu⁰ species (2102 cm⁻¹) and CO linearly-adsorbed on atomic Pt (2065 cm⁻¹), two bands at 2023 and 1853 cm⁻¹ attributed to CO linearly- and bridged-adsorbed on Pt clusters are resolved, respectively.

Additional PtCu bimetallic catalysts possessing only Pt clusters (0.9%Ptₙ/Cu-CuZrOₓ) and unique bulk PtCu alloy nanoparticles (0.9%PtCu/CuZrOₓ) were prepared by incipient wetness impregnation to introduce PtCl₆⁻ onto Cu-CuZrOₓ or CuZrOₓ followed by reduction. For 0.9%Ptₙ/Cu-CuZrOₓ, no visible Pt nanoparticles are resolved instead of Cu nanoparticles in a particles size of 3.4 nm (Fig. 3a). Pt clusters around...
Cu-CuZrOx possesses much more Pt-Pt coordination than 0.9%Pt1+4.1 Pt-Cu and 2.3 Pt-Pt coordination for 0.9%PtCu-CuZrOx, respectively. Pt1+Ptn/Cu-CuZrOx in the light of the larger asymmetric shoulder peak in 0.9%Pt1+Ptn/Cu-CuZrOx with an increased discrepancy (Fig. 2h), Pt1+Ptn/Cu-CuZrOx is the most negative-charged, and subsequently, the reference of Pt foil, the intensity of the red line indicates 0.9%Pt1/Cu-CuZrOx and 0.9%Ptn/Cu-CuZrOx shift to 2065 and 2023 cm−1 distinguished in the AC-HAADF-STEM image (Fig. 3d). In R-spaced FT-EXAFS spectra (Fig. 3e), besides Pt-Cu coordination (2.3 Å), 0.9%Ptn/Cu-CuZrOx (Fig. 3f, g) was obtained (Supplementary Fig. 9), which was then plotted as a function of the oxidation state (Fig. 3g). The Ptδ valence state has been quantified in a δ value of 1.85, 1.13, and 0.44 for 0.9%Pt1+Ptn/Cu-CuZrOx, 0.9%Pt1+Ptn/Cu-CuZrOx, and 0.9%PtCu-CuZrOx with bulk Pt foil and PtO2 as references.

Cascade synergistic activation by atomic Pt, and cluster Ptn sites

The activation of glycerol has been first investigated by in situ FT-IR spectra after the adsorption of 1-propanol for 30 min followed by desorption, which possesses only primary O-H bonds (Fig. 4). On 0.9%Pt1+Ptn/Cu-CuZrOx (Fig. 4a and Supplementary Table 3), besides the bands attributed to adsorbed bidentate 1-propanol and propoxy (marked in magenta), the bands at 2740, 2925, and 3235 cm−1 assigned to ν(C−H), ν(C−O), and δ(CH) of n2-adsorbed propoxy (marked in olive) appear. The corresponding adsorption models labeled in the same color are also displayed below. As the desorption time increased, the bands gradually decrease except for the n2-adsorbed mode, which is inferred to be stable in such a synergistic activation. While on 0.9%Pt1+Ptn/Cu-CuZrOx (Fig. 4b) or 0.9%PtCu-CuZrOx (Fig. 4c), similar absorption bands with weakened intensity for adsorbed 1-propanol, propoxy species, and n1-adsorbed propoxy peak, except that no bands for n3-adsorbed propoxy are resolved. Combined with the electronic state analysis, Ptδ−Cu bonds are responsible for the dehydrogenation of the C−H bonds as expected and the increasing electron-rich state in 0.9%Pt1+Ptn/Cu-CuZrOx.

1.2 nm (olive circle) are observed on Cu (111) planes without visible atomic Pt, other than on the oxide surface (Fig. 3b). For 0.9%PtCu-CuZrOx, PtCu alloy (111) nanoparticles with a particle size of 3.5 nm were obtained (Fig. 3c), and no visible individual Pt atoms are distinguished in the AC-HAADF-STEM image (Fig. 3d). In R-spaced FT-EXAFS spectra (Fig. 3e), besides Pt-Cu coordination (2.3 Å), 0.9%PtCu-CuZrOx possesses much more Pt-Pt coordination than 0.9%Pt1+Ptn/Cu-CuZrOx in the light of the larger asymmetric shoulder peak in the region around 2.6 Å. 0.9%Pt1+Ptn/Cu-CuZrOx exhibits one dominant peak (2.3 Å) with a tiny shoulder peak (2.6 Å), indicating Pt-Cu as the main Pt coordination with a small amount of Pt-Pt coordination. Moreover, no resolved PtO coordination is observed. As a comparison for 0.9%Pt1+Ptn/Cu-CuZrOx in 6.1 Pt-Cu and 3.0 Pt-Pt coordination, 4.1 Pt-Cu and 2.9 Pt-Pt coordination are identified for 0.9%Pt1/Cu-CuZrOx, and 4.1 Pt-Cu and 2.3 Pt-Pt coordination for 0.9%PtCu-CuZrOx, respectively (Supplementary Table 2). CO-DRIFTS spectra of the physically-mixed 0.5%Pt1+Ptn/Cu-CuZrOx, 0.9%Pt1/Cu-CuZrOx, and 0.9%PtCu-CuZrOx were collected as control (Supplementary Table 2). CO-DRIFTS spectra after the adsorption of 1-propanol for 30 min followed by desorption, which possesses only primary O-H bonds (Fig. 4). On 0.9%Pt1+Ptn/Cu-CuZrOx (Fig. 4a and Supplementary Table 3), besides the bands attributed to adsorbed bidentate 1-propanol and propoxy (marked in magenta), adsorbed monodentate propoxy (marked in blue), and n1-adsorbed propoxy (marked in red), the bands at 2740, 2925, and 3235 cm−1 assigned to ν(C−H), ν(C−O), and δ(CH) of n2-adsorbed propoxy (marked in olive) appear. The corresponding adsorption models labeled in the same color are also displayed below. As the desorption time increased, the bands gradually decrease except for the n2-adsorbed mode, which is inferred to be stable in such a synergistic activation. While on 0.9%Pt1+Ptn/Cu-CuZrOx (Fig. 4b) or 0.9%PtCu-CuZrOx (Fig. 4c), similar absorption bands with weakened intensity for adsorbed 1-propanol, propoxy species, and n1-adsorbed propoxy appear, except that no bands for n3-adsorbed propoxy are resolved. Combined with the electronic state analysis, Ptδ−Cu bonds are responsible for the dehydrogenation of the C−H bonds as expected and the increasing electron-rich state in 0.9%Pt1+Ptn/Cu-CuZrOx.
promotes the activation of the C-H bonds. Moreover, by comparing the area ratio of $\nu$(C-O) and $\nu$(C-OH) of the adsorbed bidentate 1-propanol (marked in magenta), 0.9%Pt$_1$/Cu-CuZrO$_x$ exhibits superior O-H activation beyond 0.9%Pt$_1$+Pt$_n$/Cu-CuZrO$_x$ and 0.9%Pt$_1$/Cu-CuZrO$_x$, confirming that the Pt-Pt bonds are responsible for the dehydrogenation of the primary O-H bonds to propoxy and more Pt-Pt coordination (Supplementary Table 2) is preferred. As a control, on 0.5%Pt$_1$/Cu-CuZrO$_x$ (Fig. 4d), almost no propoxy and propanal species were observed except for the adsorbed non-dissociated 1-propanol species.

Then the glycerol activation on atomic Pt$_1$ and cluster Pt$_n$ sites has been investigated (Fig. 5a and Supplementary Table 4). Taking pristine glycerol as reference (Supplementary Fig. 10a), on 0.9%Pt$_1$+Pt$_n$/Cu-CuZrO$_x$ two strong absorption bands at 1068 and 1054 cm$^{-1}$ attributed to primary $\nu$(C-O) of bidentate and monodentate dissociated glycerol (marked in magenta), a strong band at 1099 cm$^{-1}$ to the secondary $\nu$(C-OH) of non-dissociated glycerol (marked in blue), and a tiny band at 1152 cm$^{-1}$ to non-dissociated glycerol with secondary O-H group forming hydrogen bonds on the metal oxides (marked in blue) appear, indicating the dominance on the dissociated activation of the primary O-H bands. Besides $\eta^1$-adsorbed GLAD (marked in red), the bands at 2713, 1337, and 1186 cm$^{-1}$ assigned to $\nu$(CH), $\delta$(CH), and $\nu$(C-O) of $\eta^2$-adsorbed GLAD (marked in olive) appear. No visible activation of the secondary C-H bonds to dihydroxyacetone has been detected. While on 0.9%Pt$_1$/Cu-CuZrO$_x$ or 0.9%Pt$_1$/Cu-CuZrO$_x$, no obvious bands for $\eta^2$-adsorbed GLAD are observed, and only weakened primary O-H and C-H bond activation are detected. More H-bonded secondary $\nu$(C-OH) species on 0.9%Pt$_1$/Cu-CuZrO$_x$ are observed. As a control, on 0.5%Pt$_1$/Cu-CuZrO$_x$, only H-bonded secondary $\nu$(C-OH) species appear without any dissociated GLAD detected. Therefore, the dominant activation of primary O-H and C-H bonds of glycerol in $\eta^2$-GLAD mode on atomic Pt$_1$ and cluster Pt$_n$ sites has been identified, consistent with the in situ FT-IR spectra of the 1-propanol adsorption. In addition, the appearance of $\nu$(OCO) in glycerate (marked in wine) could be attributed to the adsorption of formed C=O on metal and the metal oxides.

The activation of the aldehyde group has been first investigated by in situ FT-IR spectra of the adsorption of acetaldehyde (Fig. 6). On 0.9%Pt$_1$+Pt$_n$/Cu-CuZrO$_x$ (Fig. 6a and Supplementary Table 5), the bands at 1760, 1747 and 1730 cm$^{-1}$ assigned to $\nu$(C=O) of $\eta^1$-adsorbed acetaldehyde (marked in red) and bands at 1275 and 1352 cm$^{-1}$ assigned to $\nu$(C-O) and $\delta$(CH) of $\eta^2$-adsorbed acetaldehyde (marked in olive) both appear. On 0.9%Pt$_1$/Cu-CuZrO$_x$ (Fig. 6b), similar absorption bands for $\eta^1$ and $\eta^2$-adsorbed acetaldehyde with

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**Fig. 4** | The activation of the primary O-H and C-H bonds. In situ FT-IR spectra after the adsorption of 1-propanol for 30 min followed by desorption at desorption times of 1, 5, 10, 15, and 20 min (from top to bottom) on 0.9%Pt$_1$+Pt$_n$/Cu-CuZrO$_x$ (a), 0.9%Pt$_1$/Cu-CuZrO$_x$ (b), 0.9%Pt$_1$/Cu-CuZrO$_x$ (c), and 0.5%Pt$_1$/Cu-CuZrO$_x$ (d). The simulated adsorption models are displayed corresponding to the absorption band labeled in the same color.
sharply-weakened intensity are observed, except that a broad band around 3000 cm\(^{-1}\) associated with the coupling products of adsorbed acetaldehyde appears (marked in dark yellow). As the desorption time increased, besides the band at 1352 cm\(^{-1}\) assigned to \(\delta(C-H)\) in \(\eta_2\)-acetaldehyde species on sole Pt\(_x\) sites, a band at 1345 cm\(^{-1}\) assigned to a weaker \(\delta(C-H)\) also appear, which could be generated by the stronger Pt-C interaction on more electron-deficient Pt\(_x\) sites in 0.9%Pt\(_x\)+Ptn/Cu-CuZrO\(_x\). It is envisaged that the generation of \(\eta_2\)-adsorbed acetaldehyde on atomic Pt\(_x\) and cluster Ptn sites make the C=O activation much faster and inhibits the side coupling reaction. In addition, the \(\nu(OCO)\) bands attributed to the C=O adsorption on metal sites and oxygen of metal oxides (marked in wine) also appear. For GLAD activation (Fig. 5b), taking pristine GLAD as reference (Supplementary Fig. 10b), \(\eta_1\) (marked in red) and \(\eta_2\)-adsorbed (marked in olive) GLAD species are both observed on 0.9%Pt\(_x\)+Ptn/Cu-CuZrO\(_x\), 0.9%Ptn/Cu-CuZrO\(_x\), and 0.9%PtCu-CuZrO\(_x\). On 0.9%Pt\(_x\)+Ptn/Cu-CuZrO\(_x\), \(\eta_2\)-adsorbed GLAD are dominant adsorbed species. While on 0.9%Pt\(_x\)/Cu-CuZrO\(_x\) and 0.9%PtCu-CuZrO\(_x\), \(\eta_2\)-adsorbed GLAD species appear as predominant adsorption. It is worth noting that the \(\eta_2\)-GLAD \(\nu(C-O)\) band (filled in olive) at 1196 cm\(^{-1}\) on 0.9%Pt\(_x\)/Cu-CuZrO\(_x\) displays an obvious red-shift to 1183 cm\(^{-1}\) on 0.9%Pt\(_x\)+Ptn/Cu-CuZrO\(_x\) (Fig. 5b, inset), indicating a weaker \(\nu(C-O)\) in the \(\eta_2\)-GLAD species. However, on 0.9%Pt\(_x\)+Ptn/Cu-CuZrO\(_x\) with less Pt-Pt coordination quantity in the similar Pt-Pt coordination number with 0.9%Ptn/Cu-CuZrO\(_x\) exhibits better desorption of carboxyl groups. As a control, on pristine Cu-CuZrO\(_x\) (Fig. 7d), only tiny absorption bands assigned to the vapor propionic acid were detected. Combined with the GLAD adsorption...
(Fig. 5b), it is concluded that 0.9%Pt + Pt/Cu-CuZrOx, exhibits both better activation of the aldehyde group and desorption of the carboxy group originated from the synergistic catalysis by atomic Pt and cluster Pt sites, which is envisaged to facilitate the direct transformation from GLAD to GLYA.

Cascade synergistic catalysis during in situ surface reaction

In situ time-resolved FT-IR spectra of 0.9%Pt + Pt/Cu-CuZrOx, on exposure to 1-propanol at 60°C in a flow of O2 and H2O were recorded to further elucidate the cascade synergistic catalysis and the evolution of surface adsorbed intermediates in the oxidation of glycerol to GLYA (Fig. 8a). The bands between 1600-1500 cm⁻¹ assigned to the ν(C=O) of the adsorbed propionic acid in bridging bidentate configuration appear and gradually increase with on-stream time, accompanied with the appearance of the ν(C=O) band of carboxyl groups since 15 min. It indicates that 1-propanol could be converted to propionic acid over 0.9%Pt + Pt/Cu-CuZrOx, in the presence of O2 and H2O. With on-stream time, the area ratio of ν(C=O) at 1138 cm⁻¹ of the adsorbed monodentate 1-propanol (marked in blue) to ν(C-OH) at 1165 cm⁻¹ of the adsorbed monodentate propoxy (marked in cyan) gradually increases, but that of the adsorbed monodentate 1-propanol are not so visible (marked in magenta). With on-stream time, the area ratio of the total monodentate ν(C=O) and ν(C-OH) (1138 and 1165 cm⁻¹) to the total bidentate ones (1053 and 1066 cm⁻¹) gradually decreases. It evidences that the formation of propionic acid is originated from the adsorbed monodentate 1-propanol. The ν(CH), δ(CH), and ν(C-O) bands of ν1-adsorbed propional (marked in olive) are clearly resolved without ν1-adsorbed propional bands, confirming the synergistic activation of atomic Pt and cluster Pt, on the C-H and O-H bonds, and demonstrating the ν1-adsorbed propional as the intermediates in the subsequent oxidation process to propionic acid. More importantly, the area ratio of ν(C=O) in propoxyl at 1138 cm⁻¹ (marked in blue) to ν(C=O) in ν1-mode propoxyl at 1295 cm⁻¹ (marked in olive) remarkably increased with on-stream time, indicating that the synergistic activation pathway is O-H activation on the Pt, cluster followed by the C-H activation on the atomic Pt sites. The schematic illustration of the possible surface reaction process has been displayed in Fig. 8b. In situ XANES spectroscopy, which is sensitive for measuring the chemical states of Pt and Cu, was performed to investigate their changes during the catalytic reaction (Supplementary Fig. 11). It is found that the introduction of glycerol on 0.9%Pt + Pt/Cu-CuZrOx, leads to a distinct low-energy shift of the white line peak in Pt L3-edge XANES spectra (Supplementary Fig. 11a). Then the exposure to O2 make the white line gradually return to the similar level of the fresh catalyst. As for the Cu K-edge XANES spectra after the sequential exposure to glycerol solution and O2 flow (Supplementary Fig. 11b), no visible change of the Cu adsorption edge has been observed, implying that no obvious effect on surface Cu species has been detected in the oxidation in this work. Cu species has been inferred to play a role in the electron donation to Pt atom to form Pt-Cu coordination promoting the C-H activation of glycerol during the oxidation.

The selective oxidation of glycerol on 0.9%Pt + Pt/Cu-CuZrOx using 18O2 and H218O were performed, respectively, to identify the reactive oxygen species (Supplementary Fig. 12), which were reported to participate in the oxidation process. With 18O2 labeling, 18O was not observed in the products of glycerol oxidation (Supplementary Fig. 12a). With H218O labeling, the mass spectrum shows that one or two 18O atoms were incorporated into GLYA as the main product with a small amount of GLAD or DHA as by-products (Supplementary Fig. 12b). Combining with the previous reports, it could be concluded that activated O2 and H2O were incorporated to form peroxide (OOH) and OH to abstract adsorbed C-H and O-H bonds, finally generating H2O2 and H2O (Supplementary Fig. 12c).

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Atomic Pt$_1$ enhanced C-H activation synergistic with cluster Pt$_{n}$ catalysis to promote glycerol conversion and GLYA selectivity

In the selective oxidation of glycerol in an ebullated bed with an O$_2$ flow of 30 mL/min at 60$^\circ$C, 0.9%Pt$_1$ + Pt$_{n}$/Cu-CuZrO$_x$ catalyzed the conversion of glycerol to GLYA with a selectivity of 80.2 ± 0.2% at a glycerol conversion of 90.0 ± 0.1% in 8 h (Fig. 9 and Supplementary Table 8). Over 0.9%Pt$_{n}$/Cu-CuZrO$_x$ and 0.9%PtCu-CuZrO$_x$, a GLYA selectivity of 66.9% at a glycerol conversion of 85.6%, and a GLYA selectivity of 60.6% at a glycerol conversion of 65.0% were achieved. While 0.5%Pt$_1$/Cu-CuZrO$_x$ only gives a very low conversion of 3.7% with a GLYA selectivity of 64.1% (Supplementary Fig. 13a) and do not change with time. As a control, the activity of Cu-CuZrO$_x$ is negligible (0.4%) with oxalic acid (OA) and formic acid (FA) as main products (Supplementary Fig. 13b). It indicates that the cooperation of atomic Pt$_1$ with cluster Pt$_{n}$ promotes the glycerol conversion (Fig. 9a). In the profile of the reaction rate towards the Pt valence state (Fig. 9b), a good linear relationship between the activity and the Pt electron-rich state displays, further confirming the enhanced C-H activation by atomic Pt$_1$ leads to promoted glycerol conversion. When 0.9%Pt$_1$ + Pt$_{n}$/Cu-CuZrO$_x$ was pretreated by N$_2$O to poison the surface Cu sites (0.9%Pt$_1$ + Pt$_{n}$/Cu-CuZrO$_x$-N$_2$O), sharply-declined glycerol conversion to 70.0% further supporting the enhanced C-H activation by atomic Pt$_1$ sites (Supplementary Table 8). To ensure that the catalytic experiments were performed under the regime of kinetic control, Mears and Weisz–Prater analyses$^{62-65}$ were employed to investigate the mass transfer based on the reaction rates in our work (Supplementary Table 9). The calculated values of the Mears criterion are $7.74 \times 10^{-5}$, $5.57 \times 10^{-5}$, and $4.31 \times 10^{-5}$ on 0.9%Pt$_1$ + Pt$_{n}$/Cu-CuZrO$_x$, 0.9%Pt$_{n}$/Cu-CuZrO$_x$, and 0.9%PtCu-CuZrO$_x$, respectively, far smaller than 0.15, implying that external mass transfer effects can be neglected. The calculated values of the Weisz–Prater Criterion are $2.96 \times 10^{-9}$, $2.32 \times 10^{-9}$, and $1.18 \times 10^{-9}$ on 0.9%Pt$_1$ + Pt$_{n}$/Cu-CuZrO$_x$, 0.9%Pt$_{n}$/Cu-CuZrO$_x$, and 0.9%PtCu-CuZrO$_x$, respectively, far smaller than 1, implying that internal mass transfer effects can also be neglected.

Over 0.9%Pt$_1$ + Pt$_{n}$/Cu-CuZrO$_x$, the GLYA selectivity holds at 80.4% along the increasing time, with a small amount of glyceraldehyde (5.3%) and DHA (9.5%) (Supplementary Fig. 14a). No obvious GLAD accumulation or transformation is observed along with the increasing reaction time, indicating a fast conversion from GLAD to GLYA. GLYA selectivity over 0.9%Pt$_{n}$/Cu-CuZrO$_x$ slightly increases along with the reaction time and reaches 66.7% at 4 h with 10.6% GLAD, 11.9% of DHA, and 5.4% of acetic acid (HAc) (Supplementary Fig. 14b).
0.9%PtCu-CuZrOx, it gradually increases and reaches 60.6% at 6 h with 9.5% of GLAD, 12.6% of DHA, and 9.6% of HAc (Supplementary Fig. 14c). An obvious transformation from GLAD to GLYA is observed along with the increasing time over 0.9%Pt1+Ptn/Cu-CuZrOx and 0.9%PtCu-CuZrOx, demonstrating much slower rate of the GLAD oxidation to GLYA than that from glycerol to GLAD. At similar glycerol conversion (Fig. 9c), the GLYA selectivity over 0.9%Pt1+Ptn/Cu-CuZrOx (80.2 ± 0.2%), ascribed to the poorer transformation from GLAD to GLYA and more C-C cleavage to HAc. Over 0.9%Pt1+Ptn/Cu-CuZrOx-N2O, a sharp decline in the GLYA selectivity to 67.9% with an increased GLAD selectivity of 18.2% confirms that Ptδ–Cu bonds play a key role in the C-H activation from GLAD to GLYA. Moreover, it is worth noting that similar DHA selectivity over 0.9%Pt1+Ptn/Cu-CuZrOx (10.0 ± 0.5%), 0.9%Ptn/Cu-CuZrOx (11.9%), and 0.9%PtCu-CuZrOx (12.6%) was detected, respectively (Supplementary Table 8). According to our recent work, an isotope labeling experiment using deuterium labeling of glycerol in the secondary C-H bond was performed and DHA was side-produced from the direct activation of secondary O-H bonds in glycerol (Supplementary Fig. 15).

The selective oxidation of glycerol over 0.9%Pt1+Ptn/Cu-CuZrOx under tailored reaction conditions has been performed (Supplementary Table 10). Under the O2 flow rate of 30 (entry 1), 60 (entry 2), or 150 mL/min (entry 3), the glycerol conversion and GLYA selectivity hold at the same value, further confirming the absence of the mass transfer. Under the glycerol/Pt (mol/mol) of 300 (entry 1), 500 (entry 4), 650 (entry 5), and 1000 (entry 6), the glycerol conversion gradually declined at a similar reaction rate between 157–160 molgl molPt−1 h−1 and the GLYA selectivity slightly increases with decreased GLAD and DHA selectivity. Under the glycerol/Pt (mol/mol) of 1000, a GLYA selectivity of 84.4% at a glycerol conversion of 79.8% is obtained. Moreover, under increased glycerol concentration to 0.3 M, a GLYA selectivity of 82.3% at a declined glycerol conversion of 80.0% is achieved.

Fig. 8 | Schematic diagram of the reaction pathway during in situ surface reaction. a In situ time-resolved FT-IR spectra of 0.9%Pt1+Ptn/Cu-CuZrOx on exposure to 1-propanol at 60 °C was recorded in the presence of O2 and H2O. From bottom to top: 1, 5, 10, 15, 20, 25, and 30 min. Adsorbates were introduced to the chamber by bubbling the 1-propanol aqueous solution with O2/Ar (v/v = 1:5) flow (40 mL/min). b Proposed surface reaction process on the oxidation of 1-propanol to propionic acid.
CuZrOx (Supplementary Figs. 17 and 18) indicate that the dispersion, of our knowledge, is higher than the reports under the same condition. Compared to the cluster/nanoparticles Pt sites, the catalyst was separated by simple filtration and subsequently used without any treatment. Both the glycerol conversion and the GLYA selectivity are well preserved after five runs (Supplementary Fig. 16a). Almost no Pt leaching from the solid catalyst or no Pt presence in the spent reaction solution was detected (Supplementary Fig. 16b). 4.7 and 3.8% Pt leaching from the solid catalyst or no Pt presence in the spent catalyst or no Pt presence in the spent reaction solution were determined to be 4.2 and 3.6%, consistent with the loss in a solid catalyst. The HRTEM images, the AC-HAADF-STEM images, and the Pt L3-edge FT-EXAFS spectra of the spent 0.9%Pt1 + Ptn/Cu-CuZrOx (Supplementary Figs. 17 and 18) indicate that the dispersion, the coordination and the electronic state of Pt active sites have been well retained compared to the fresh catalyst. In the Cu 2p3/2 XPS spectra and X-ray induced Cu Auger electron spectra of the spent Pt1 + Pt/Cu-CuZrOx (Supplementary Fig. 19), the electronic state of Cu species displays no obvious change. The surface Pt/Cu molar ratio increases from 1/15 in the fresh 0.9%Pt1 + Pt/Cu-CuZrOx to 1/4 and the Cu2/Cu10 molar ratio decreases from 1/4 to 1/5. Considering no Pt leaching is detected, the slight Cu leaching is deduced to be originated from the Cu2+ species by the chelation of acid production. 

In conclusion, this work proposes and confirms a cascade synergistic catalysis of atomic Pt1 and cluster Pt, for the cascade oxidation of glycerol to GLYA, employing Pt1 + Pt/Cu-CuZrOx integrated by atomic Pt1 and cluster Pt, compared to the cluster/nanoparticles Pt sites, the enhanced C-H activation in the cascade oxidation by the atomic Pt1 in the synergistic catalysis contributes to the simultaneous high glycerol activity and high GLYA selectivity. This work not only paves an alternative strategy for promoting the cascade catalysis by engineering the surface metal active sites but also presents a green and efficient value-added routine from glycerol as industrial by-products. Further work in our lab is still underway to explore multi-synergistic catalysis to further realize the accurate activation in the primary position of polyols.

Methods

General information

Unless otherwise noted, all chemicals were purchased and used without further purification.

Catalyst preparation

As a precursor, the mixed copper and zirconium oxide was prepared by a hydrothermal method. Typically, a mixture solution of 150 mL of Cu(NO3)2·6H2O (0.03 mol) and ZrOCl2·8H2O (0.015 mol) aqueous solution, and 150 mL of CO(NH2)2 (0.113 mol) aqueous solution was stirred in a three-necked flask for 2 h, and then cooled down to room temperature to produce Cu1Zr4.3O9.6. Supported Cu sample was prepared by a reduction of Cu1Zr4.3O9.6 in an H2 stream at 350°C (heating rate: 5°C min−1) for 2 h and then cooled down to room temperature to produce Cu-CuZrOx. Supported PtCu samples with varied Pt loadings were prepared via a galvanic replacement method, as illustrated in Supplementary Experimental details. In a typical procedure, the fresh Cu-CuZrOx sample (0.5 g) was dispersed in deoxygenated deionized water (5 mL). After stirring for 0.5 h, the mixture was sealed in a Teflon-lined stainless-steel autoclave, followed by aging at 200°C for 48 h. The resulting precipitate was centrifuged, washed with deionized water, and dried at 60°C overnight. The solid was calcined in air at 450°C (heating rate: 5°C min−1) for 2 h and then cooled down to produce Cu1Zr4.3O9.6. Supported Cu sample was prepared by a reduction treatment of Cu1Zr4.3O9.6 in an H2 stream at 350°C (heating rate: 5°C min−1) for 2 h and then cooled down to room temperature to produce Cu-CuZrOx. Supported PtCu samples with varied Pt loadings were prepared via a galvanic replacement method, as illustrated in Supplementary Experimental details. In a typical procedure, the fresh Cu-CuZrOx sample (0.5 g) was dispersed in deoxygenated deionized water (5 mL), followed by dropwise adding desired concentration of H2PtCl6 solution (1 mL) in the N2 atmosphere under vigorous stirring (700 rpm) and then under reflux for 2 h. The resulting slurry was centrifuged, washed thoroughly with deoxygenated deionized water.
CuZrOx and 0.9%Pt1 +Pt/Cu-CuZrOx, respectively, combined with the surface area was calculated by the BET method. The solid was outgassed at 300 °C to remove the impurities absorbed on the surface and then Ar (40 mL min⁻¹) for 1 h. TEM and HRTEM images were performed on a FEI Tecnai G2 F30 S-TWIN transmission electron microscope equipped with a Gatan GIF Quantum energy dispersive spectrometer (EDS). XRPD patterns were collected with a scanning angle range from 3° to 80° at a scan speed of 5° min⁻¹. Quantitative analysis for metal elements was performed on a Shimadzu ICPS-7300 inductively coupled plasma emission spectrometer (ICP-ES). Typically, approximately 2.0 mg of solid was dissolved in aqua regia and diluted for metal elements analysis. For S, P, N, O, and F determination, an external calibration method was used. The gaseous product was collected and identified by GC equipped with a TDX-1 column and TCD detector. CO2 was used. The gaseous product was collected and identified by GC equipped with a TDX-1 column and TCD detector. CO2 was used. The gas was produced by bubbling Ar through the solution at 30°C. H2 was used. The gas was collected for further analysis. The gas was produced by bubbling Ar through the solution at 30°C. H2 was used. The gas was collected for further analysis. The gas was produced by bubbling Ar through the solution at 30°C. H2 was used. The gas was collected for further analysis.

Characterizations
XRD measurements were performed on a Shimadzu XRD-6000 diffractometer using Cu Kα radiation (λ = 0.1541 nm) and operated at 40 kV and 30 mA. XRD patterns were collected with a scanning angle (2θ) range from 3° to 80° at a scan speed of 5° min⁻¹. Quantitative analysis for metal elements was performed on a Shimadzu ICPS-7300 inductively coupled plasma emission spectrometer (ICP-ES). Typically, approximately 2.0 mg of solid was dissolved in aqua regia and diluted to 10 mL in a volumetric flask before characterization. N₂ adsorption was performed on a Quantachrome Autosorb-IC-VP analyzer to determine the specific surface area and the porosity. The specific surface area was calculated by the BET method. The solid was outgassed in a flow of N₂ at 100°C for 5 h prior to the measurement. H₂-TPR was carried out on a Micromeritics ASAP 2010 equipped with a TCD detector. FESEM image was collected on a Zeiss EVO-18 scanning electron microscope. TEM and HRTEM images were collected on a Tecnai G2 F30 S-TWIN transmission electron microscope equipped with an EDAX XFlash 4000 energy dispersive spectrometer (EDS). Images were collected on a JEM-ARM 200F electron microscope equipped with a Si detector and an EELS detector. XPS characterization was performed on a Shimadzu XPS-7300 equipped with a monochromatic Al Kα source (λ = 1486.6 eV) and measured at a pass energy of 100 eV. The core-level spectra were analyzed using a Shirley-type background subtraction. FT-IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer equipped with a MCT detector and a series of ATR accessories. The spectra were collected at 25°C. To avoid the adsorbate condensation, the BaF₂ windows should be pretreated at 70°C.

In situ FT-IR study
The adsorption/desorption of 1-propanol, acetaldehyde, and propionic acid on supported PtCu samples were recorded on a Nicolet iS50 spectrometer equipped with a cell fitted with BaF₂ windows and an MCT-A detector cooled by liquid nitrogen. The spectrum was collected at a resolution of 4 cm⁻¹ with an accumulation of 64 scans in the range of 4000–750 cm⁻¹. Approximately 20 mg of solid sample was pressed into a self-supported wafer in each measurement. Then, the sample wafer was pretreated under a flow of H2/Ar (vv = 1:4) for 30 min at 300°C to remove the impurities absorbed on the surface and then cooled to 20°C. The background was collected at 20°C under a flow of Ar (40 mL min⁻¹) before the adsorbate introduction. 1-propanol, acetaldehyde, or propionic acid was introduced by bubbling pristine adsorbate liquid by a flow of Ar (40 mL min⁻¹) at 20°C for 30 min to obtain a stable spectrum. Then, the system was purged with a flow of Ar (40 mL min⁻¹), and the desorption spectra were recorded towards the desorption time until there was no change in the band intensity. For in situ time-resolved FT-IR spectra of 0.9%Pt1 +Pt/Cu-CuZrOx on exposure to 1-propanol at 60°C in a flow of O₂ and H₂O. Adsorbates were introduced to the chamber by bubbling 1-propanol aqueous solution (water content: 1 wt%) by a flow of O₂/Ar (vv = 1:5). As for the adsorption of CO, the sample was exposed to a flow of CO/He (vv = 1:9) at 20°C for 30 min. The adsorption of glycerol and glyceraldehyde on supported PtCu samples were recorded on a VERTEX70 FT-IR spectrometer equipped with a cell fitted with BaF₂ windows and a photo voltaic MCT detector. Considering the high boiling point, glycerol or glyceraldehyde was pre-heated at 60°C and then introduced by a flow of Ar (40 mL min⁻¹) for 5 min. The spectra were collected at 25°C. To avoid the adsorbate condensation, the BaF₂ windows should be pretreated at 70°C.

Catalytic evaluation
The catalytic oxidation of glycerol/GLAD was conducted in an ebullated bed. In a typical procedure, 15 mL of an aqueous glycerol solution (0.1 M) and a proper amount of catalyst in powder form with an initial molar glycerol/Pt ratio of 300 were loaded into an ebullated bed. During the oxidation reaction, O₂ (99.9%) was introduced into the reactor at 30 mL min⁻¹ via a mass flow controller at atmospheric pressure. The reaction time of zero was defined when the temperature of the reaction mixture reached 60°C (heating rate: 10°C min⁻¹). After the reaction, the liquid products were analyzed by an Agilent 7890A GC equipped with both UV detector and FID detector. An Aminex HPX 87H column (Bio-Rad, 300 × 7.8 mm) operating at 50°C was used with 10 mM aqueous H₂SO₄ or HCOOH as the eluent at a flow of 0.5 mL min⁻¹. For quantification, an external calibration method was used. The gaseous product was collected and identified on a Shimadzu GC-2014C GC equipped with a TDX-1 column and TCD detector. CO₂ was identified as the only gaseous product. Catalytic performance towards the selective oxidation of glycerol over 0.9%Pt1 +Pt/Cu-CuZrOx under tailored reaction conditions was carried out. 0.9%Pt1 +Pt/Cu-CuZrOx was recycled by simple filtration and subsequently used in the next catalytic cycle without further purification or any treatment. The catalytic oxidation of GLAD was conducted in a similar procedure.

Labeling experiments
Reactions with deuterium-labeled glycerol, [²H₂]O₂, and H₂O were performed using 3 mL of glycerol and 0.01 g of catalyst. A liquid chromatograph equipped with a Quattro Premier XE mass spectrometer was used to identify the formed labeled products. To verify the formation of H₂O₂, a mixed solution (abbreviated as P) of phosphate buffer, N, N-diethylbenzene-1,4-diamine sulfate, and horseradish peroxidase was added to a fresh reaction solution after catalyst separation. Reference solutions of H₂O₂ (0.05 M), glycerol (0.1 M), GLYA (0.1 M), GLAD (0.1 M), DHA (0.1 M), TTA (0.1 M), GCA (0.1 M), OA (0.1 M), HAc (0.1 M), and FA (0.1 M) were used.

Data availability
The data supporting this study are available within the paper and the Supplementary Information. All other relevant source data are available from the corresponding author upon reasonable request.

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Author contributions

J.H. and Z.A. conceived the idea and directed the research. Z.A. wrote the manuscript and performed in situ FT-IR and in situ EXAFS; Z.Z. carried out the catalyst preparations, the characterization, and the catalytic evaluations; Z.H. reproduced some catalytic evaluations; H.H. conducted the isotope labeling experiments; B.S. conducted the catalytic evaluations under tailored conditions; J.Z. helped analyze the in situ FT-IR data; Q.P. contributed to the structural simulation; Y.Z. and H.S. participated in the data analysis; B.W. contributed to in situ FT-IR; L.Z. contributed to the EXAFS analysis. All the authors commented on the manuscript and have given approval for the final version of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information

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