Switchable Structure Promoted Leaching Free Atomically Dispersed Pt Catalyst for Low Carbon Biomass Polyol Oxidation

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Abstract

Achieving efficient catalytic conversion over heterogeneous catalyst with excellent resistance against leaching is still a grand challenge for sustainable chemical synthesis in aqueous solution. Herein, we devised a leaching free atomically dispersed Pt₁/hydroxyapatite (HAP) catalyst with unique switchable structure via a simple and green in-situ anchoring strategy. Gratifyingly, this robust Pt₁/HAP catalyst exhibits remarkable catalytic selectivity and catalyst stability for the selective oxidation of C₂-C₄ bio-polyols (e.g., ethylene glycol, propanediol, glycerol and butanediol) to corresponding primary hydroxy acids. X-ray absorption spectroscopy, in-situ Fourier Transform infrared spectroscopy, density functional theory calculation and kinetics study elucidated that the switchable Pt-(O-P) linkages with strong electronic-withdrawing function of PO₄³⁻ (Pt₁-OPO₄³⁻ active site) not only realize the activation of C-H bond, but also destabilize the transition state from adsorbed hydroxy acids toward the C-C cleavage, resulting in the sharply increased selectivity of hydroxy acids. Moreover, the strong PO₄³⁻-coordination effect, originating from the enhanced interaction between positively charged Pt₁ and negatively charged OPO₄³⁻, provides electrostatic stabilization for the atomically dispersed Pt, ensuring the highly efficient catalysis of Pt₁/HAP for over 160 hours without metal leaching. This finding opens up new opportunities for efficient upgrading of bio-polyols over atomically dispersed catalysts.

Introduction

Atomically dispersed catalysts provide a new, vast and fascinating opportunity for heterogeneous catalysis due to their uniform active sites, maximum atom utilization efficiency and distinct electronic properties.^{1,2} Moreover, the atomically dispersed catalysts could be employed as an ideal model to investigate the potential structure-activity relationship at the atomic level by combining experimental characterizations and theoretical calculations.³⁻¹⁰ To date, various strategies for the preparation of the atomically dispersed catalyst (especially Pt) have been explored, such as precipitation, impregnation, coordination of heteropolyacids or ionic liquids and stabilization of organic polymer or metal-organic frameworks.¹¹⁻¹⁷ On this basis, further exploring efficient and simple synthesis protocols with environmentally friendly solvents is one of the key development direction for atomically dispersed catalysts. In addition, the atomically dispersed catalysts have been successfully applied in many catalytic reactions of small molecules (including CO, CO₂ and CH₄, etc.).¹⁸⁻²² Nevertheless, it is still a grand challenge to extend the application of atomically dispersed catalysts to complex catalytic systems with multi-step reactions, such as biomass polyol oxidation system. Consequently, developing green and convenient synthesis methods and realizing stable and efficient catalysis in more catalytic reactions pertinent to sustainable chemistry are of great significance for the development of atomically dispersed catalysts.

Primary hydroxyl acids with low carbon numbers (including glycolic acid, lactic acid and glyceric acid, etc) are critical organic chemical raw chemicals and intermediate in food, medicine, daily necessities and

other industries.^{23–27} Currently, the industrialized processes for hydroxyl acid production are mainly realized via homogeneous catalytic oxidation, nitrile hydrolysis or biological fermentation, limited by serious environmental pollution or a long production cycle.^{28–31} Recently, green heterogeneous reaction of direct aqueous phase oxidation of biomass polyols over supported noble metals (Pt, Pd, Ru and Au) under mild conditions using oxygen as green oxygenate attracted much attention.^{32,33} However, the catalytic selectivity for primary hydroxyl acid is still limited due to the uncontrollable oxidation side reaction (such as C-C bond cleavage) over metal active sites, and atomic utilization of existing catalysts remains yet to be improved.^{34–37} Meanwhile, under aqueous phase conditions, the metal leaching is a formidable challenge in production of fine chemicals and pharmaceutical intermediates, as well as in biomass conversion processes. These issues greatly hinder the further industrialization of the green oxidation process. In this scenario, unlocking the potential of atomically dispersed catalysts with the stable coordination environment, uniform active sites and maximum atomic utilization efficiency may realize the non-leaching of noble metals and improve the selectivity of primary hydroxyl acids. Nonetheless, up to now, the selective oxidation of polyols over robust atomically dispersed catalysts and the understanding of its oxidation mechanism are largely unexplored.

In this work, we first report a novel synthetic strategy of leaching free and atomically dispersed Pt catalysts for polyol oxidation. The hydroxyapatite (HAP) support provides sufficient stabilization during the in-situ anchoring process, leading to the formation of atomically dispersed Pt atoms with excellent resistance against leaching. Thanks to the strong coordination effect of PO_4^{3-} , the switchable Pt-(O-P) linkages induce the formation of $\text{Pt}_1\text{-OPO}_4^{3-}$ active sites in Pt_1/HAP catalyst, realizing the activation of C-H bond of the key oxygen-containing intermediate and preventing the C-C bond cleavage of hydroxy acid product. This work opens a new paradigm of catalysts for catalytic upgrading of biomass derived compounds.

Results And Discussion

The in-situ anchoring method for atomically dispersed Pt_1/HAP includes only one step. In brief (Figure 1a), Pt and P precursors were premixed and precipitated by $\text{NH}_3\cdot\text{H}_2\text{O}$ at 0°C, and then crystallized at a certain temperature together with Ca precursor. The as-formed sample was calcined in air and reduced (in 10 vol% hydrogen flow) to obtain the Pt_1/HAP

catalyst. X-ray diffraction (XRD) patterns show that standard HAP material $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ is successfully synthesized³⁸, and no characteristic peak of Pt is observed, suggesting a highly dispersed Pt species (Figure S1). Energy dispersive X-ray spectroscopy (EDX) mapping shows that O, P, Ca and Pt elements are uniformly distributed in the HAP support (Figure 1b). Furthermore, aberration-corrected scanning transmission electron microscopy with high-angle annular dark-field (HAADF-STEM) in Figure 1c reveals that although few tiny Pt clusters are generated on rod-shaped HAP support, atomically dispersed Pt is absolutely dominant in Pt_1/HAP . Control experiments confirm that the atomically dispersed Pt is formed on Pt_1/HAP with the metal loading of 0.14 wt% (Table S1), while Pt nanoparticles

are formed with higher Pt loading (Figure S2). Meanwhile, N₂ physisorption results show that both HAP and Pt₁/HAP possess typical isotherms of type-IV with the D-shaped tapered hole and similar Brunauer-Emmett-Teller surface area (approximately 50 m²/g) and pore volume (approximately 0.4 cm³/g), indicating that the incorporation of Pt does not affect the physical structure of HAP support (Figure S3 and Table S1).³⁹ On these foundations, it can be preliminarily concluded that atomically dispersed Pt atoms are formed in Pt₁/HAP via the in-situ anchoring method.

Coordination environment of Pt species on HAP was studied by extended X-ray absorption fine structure (EXAFS). From the k^3 -weighted Fourier transform (FT) spectra (Figure 2a), only one main peak located at approximately 1.8 Å is observed, corresponding to the Pt-O shell.⁴⁰ Compared with Pt foil and PtO₂, no Pt-Pt coordination peak (located at approximately 2.7 Å) is detected.⁴⁰ The EXAFS fitting results including the first shell coordination parameters, structure and bond length were summarized in Table S2. Pt₁/HAP catalyst displays a Pt-O coordination number of 5 in the first shell of the Pt atom, which was different from the results on standard Pt foil (12) and PtO₂ (6) samples.⁴¹ Density functional theory (DFT) calculations were employed to better understand the coordination state of isolated Pt atoms. Periodical HAP (001) was selected as the support in the calculation model due to its easily exposed crystal surface (Figure S4-S5 and Figure 2b). The optimized structure (Figure S4) shows that an isolated Pt atom replaces Ca²⁺ and is surrounded by five O atoms in three PO₄³⁻ ligand with the formation of five Pt-O-P linkages. Moreover, Pt-O bond lengths range from 1.96 to 2.09 Å, which is in good agreement with the EXAFS fitting results. In addition, the Pt and surrounding PO₄³⁻ ligands display a quasi-square-planar geometry, and the binding energy of Pt atom on the HAP (001) is as high as -3.51 eV.⁴² These indicate that PO₄³⁻ ligand in the HAP support plays a vital role in the stabilization of isolated Pt atom. Figure 2c shows that the intensity maxima in a k space of 6-10 Å⁻¹ and 4-8 Å⁻¹ are assigned to Pt-Pt (in Pt foil) and Pt-O contributions (in PtO₂), respectively. Pt₁/HAP exhibits only one maximum intensity lobe near 6 Å⁻¹ (Pt-O). The WT representations obtained for Pt₁/HAP catalyst show a main lobe at low R values in the k space of 2-6 Å⁻¹. However, the R and k values of Pt₁/HAP catalyst are slightly different from that of PtO₂. The evident elongation of the first lobe toward small R and k -values should be related to O atoms coordinated with isolated Pt atom in HAP structure. The suber lob in the large R values (2-3 Å⁻¹) in the k space of 2-4 Å⁻¹ can be assigned to the lighter element scattering such as O in PtO₂. The suber lob is found in a similar k space for Pt₁/HAP, but the lob shows much weaker and lower R value compared to PtO₂, due to the different O environment in PO₄³⁻ ligand compared to the one of PtO₂. Consequently, EXAFS and HAADF-STEM strongly confirm that atomically dispersed Pt₁/HAP catalyst is successfully prepared by in-situ anchoring method.

In the synthesis process of Pt₁/HAP, low-temperature in-situ doping method was employed to avoid the introduction of other environmentally unfriendly or expensive solvents. We envisaged that HAP support could stabilize isolated Pt atoms for several reasons: 1) HAP is constructed by the phosphate tetrahedral

group (PO_4^{3-}), Ca^{2+} (surrounded by PO_4^{3-}) and OH^- (neutralizing positive charge). Part of the internal cation (mainly the Ca^{2+}) can be replaced by partial positively charged Pt to keep the balance of charge and space structure, thus the stable crystal structure $[\text{Ca}_{10-x}\text{Pt}_x(\text{PO}_4)_6(\text{OH})_2]$ remains unchanged. Therefore, Pt precursor can be uniformly doped into the crystal of HAP during crystallization^{43,44}. Meanwhile, due to the smaller radial size of Pt (94 Å) [compared with Ca^{2+} (100 Å)], the overall XRD peak position of Pt_1/HAP shifts to a lower angle, resulting in the smaller lattice constant (Figure S1). 2) Fourier Transform infrared spectroscopy (FT-IR) spectra strongly confirm the typical and stable PO_4^{3-} structure in the HAP support and Pt_1/HAP (Figure S6). The existence of PO_4^{3-} ligand with stable tetrahedral characteristics could provide electrostatic stabilization for single-atom species, leading to the formation of five Pt-O-P linkages.³⁹ This PO_4^{3-} coordination effect of HAP with the formation of Pt-O-P linkages creates an ideal prerequisite for the formation of atomically dispersed Pt. Under the influence of these two factors, the isolated Pt atoms can exist stably in Pt_1/HAP .

X-ray absorption near edge structure (XANES) was further carried out to determine the electronic interactions between Pt atom and HAP (Figure 2d). The Pt white-line intensity for the Pt_1/HAP catalyst near 11568 eV⁴⁵ (1.59 eV) is lower than that of PtO_2 (2.23 eV), but higher than that of Pt foil (1.24 eV). This indicates that isolated Pt atom is partial positively charged. Mulliken charge obtained by DFT calculation (Figure 2b) also confirms the electron transfer from Pt to PO_4^{3-} ligands, resulting in a positive charge of 0.41 |e| for Pt atom and the negative charge of ~ -1.0 |e| for PO_4^{3-} ligands.⁴⁰ Therefore, XANES and DFT calculation reveal that the stable PO_4^{3-} ligand processes strong electronic-withdrawing function in Pt_1/HAP . This partial positively charge state of Pt atoms caused by covalently bonded with PO_4^{3-} may exhibit distinctive catalytic performance due to the formation of electronic coupled Pt-(O-P) linkages.

Subsequently, the structure of atomically dispersed Pt_1/HAP catalyst on the reduction properties and chemical adsorption was analyzed. H_2 -temperature-programmed reduction (TPR) profile of unreduced Pt_1/HAP only exhibits an extremely weak reduction peak for metallic Pt at approximately 200°C (Figure 2e-1 and Figure S7). Table S3 shows that the H_2 consumption of Pt in Pt_1/HAP is only 0.7 $\mu\text{mol/g}$, and the ratio of H_2 to Pt (< 300°C) is only 0.05, which is much lower than that of Pt/AC (2.56). This indicates that the isolated Pt atoms have entered into the framework of HAP, and Pt-O-P bond is strong in the HAP structure.⁴⁶ Meanwhile, Pt_1/HAP and HAP exhibit almost the same NH_3 temperature-programmed desorption (NH_3 -TPD) profiles (Figure <link rid="fig2">2</link>e-2 and Figure S8), suggesting that the introduction of atomically dispersed Pt atoms have no significant effect on the acidity of HAP. Nevertheless, Figure 2e-3 shows that the desorption peak of CO_2 -TPD of Pt_1/HAP catalyst at $\sim 220^\circ\text{C}$ (medium basic sites) is lower than that of HAP, while the desorption peak at $\sim 150^\circ\text{C}$ (weak basic sites) increases. The chemisorption of CO_2 is realized through the interaction with Lewis base of O sites.^{47,48} It is highly possible that the replacement of Ca^{2+} could significantly lower the basicity of O near Pt atoms, leading to the increase of weak basic sites on Pt_1/HAP (Figure S8 and Table S4). On these foundations, it

can be concluded that partial positively charged Pt atoms are coordinated and stabilized by PO_4^{3-} ligand of HAP, resulting in the significant change of reduction property and basic site of Pt_1/HAP .

To further understand the interaction between Pt atom and the structure of HAP, in-situ diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) and CO-TPD were performed. The DRIFTS spectra of Pt/AC (Figure 2f-1) reveal two sets of CO absorption bands centered at $2100\text{--}2200\text{ cm}^{-1}$ and $2060\text{--}2100\text{ cm}^{-1}$, which could be assigned to the CO gas and CO molecules linearly adsorbed in an a-top geometry on Pt nanoparticles (NPs) respectively. In contrast, Figure [2f-2](#) shows that Pt_1/HAP displays weak CO adsorption peaks. Meanwhile, CO-TPD in Figure 2g clearly shows that Pt/AC has a stronger CO desorption peak located at $\sim 110^\circ\text{C}$, while Pt_1/HAP has almost the same CO adsorption quantity as the HAP support (Table S5). Commonly, the coordination environment near positively charged Pt could result in the suppression of adsorption of CO molecule along with the electron transfer between metal and support.^{49–51} XANES and DFT calculation in this work also demonstrated the electron transfer from Pt_1 atom to PO_4^{3-} ligand in Pt_1/HAP . Consequently, DRIFTS and CO-TPD suggest the strong PO_4^{3-} -coordination effect in Pt_1/HAP .

Selective oxidation of primary hydroxyl group in polyols, which is schematically illustrated in Figure 3a, was conducted. Initially, oxidation of glycerol was performed under mild conditions, given that good catalytic performance was previously obtained on Pt based catalysts.⁵² Negligible products are obtained using the HAP support, while both Pt/AC and Pt_1/HAP are active for glycerol oxidation. The final conversion and selectivity are presented in Figure 3b. The Pt mass based initial reaction rate of Pt_1/HAP ($1.8\text{ mol/g}_{\text{Pt}}/\text{h}$) is almost four times higher than that of Pt/AC ($0.4\text{ mol/g}_{\text{Pt}}/\text{h}$). However, the turnover frequency (TOF) values on Pt/AC and Pt_1/HAP are almost identical (Table S6), indicating that the site activity for glycerol oxidation is similar for the two catalysts, although the active sites are very different. The high initial reaction rate of Pt_1/HAP based on Pt mass is mostly attributed to the high accessible Pt atom. Furthermore, the glyceric acid selectivity of Pt_1/HAP (86.7%) is nearly twice as high as that of Pt/AC (47.8%), and a record high yield of glyceric acid up to 80.2% is obtained on Pt_1/HAP . Considering the difference of by-product selectivity between Pt/AC and Pt_1/HAP (Table S6), the remarkable glyceric acid yield is probably because that the isolated Pt atom active sites could selectively oxidize glycerol to carboxylic acids by

suppressing the C-C bond cleavage to form C1 and C2 acids. We further extended the application of Pt_1/HAP to the oxidation of ethylene glycol, 1,2-propylene glycol and 1,2-butanediol (Figure 3c-e and Table S7-S9). Obviously, the selectivity of the corresponding hydroxy acid products is also significantly improved on Pt_1/HAP compared to Pt nanoparticles on Pt/AC for all the reactions tested here. The results illustrate the atomically dispersed catalyst Pt_1/HAP is active and selective for low carbon polyol oxidation to the corresponding acids in general. To the best of our knowledge, this is the first successful example of atomically dispersed catalysts with excellent catalytic performance in polyol oxidation system.

Moreover, the Pt₁/HAP catalyst has substantially better stability in glycerol oxidation compared to Pt/AC. As shown in Figure 3f, the yield of glyceric acid over Pt/AC rapidly decreases with the increase of recycle times. In sharp contrast, the yield of glyceric acid over Pt₁/HAP is almost constant (~ 80%) in the first ten recycles, and then it decreases slowly. It is worth mentioning that after 20 recycles (320 h), the yield of glyceric acid is still higher than 65%, which is even higher yields achieved than some fresh catalysts reported in literature (Table S10). Moreover, the deactivation factor of φ on Pt₁/HAP (0.81) is almost twice that of Pt/AC (0.44) after 20 cycles. This indicates that Pt₁/HAP effect could be used as a robust and efficient catalyst for the enhanced selective oxidation of low carbon polyols. The deactivation mechanism of catalysts was studied by characterization of used catalysts. The Pt particle size of Pt/AC increased significantly from 3.9 nm to 10.0 nm after 20 cycles, while only very small nanoparticles formed on Pt₁/HAP (Figure S9). Inductively coupled plasma optical emission spectrometry (ICP-OES) revealed that the Pt metal in Pt/AC is leached seriously during the recycle test (the metal loading decreased from 0.84 wt% to 0.43 wt%), while the Pt metal loading remains almost unchanged (~ 0.14 wt%) before and after recycle test. The dissolution and re-desorption of Pt from the nanoparticles during the leaching process could be the main reason for the particle growth because the reaction temperature is too low for sintering.⁵³ FT-IR spectra show that used Pt₁/HAP (after 20 recycles) still exhibits almost the same transmission characteristic peaks belonging to PO₄³⁻ as fresh Pt₁/HAP. It suggests that the strong PO₄³⁻-coordination effect stabilizes atomically dispersed Pt atoms, thus avoiding the Pt metal leaching. Therefore, Pt₁/HAP successfully realized noble metal free leaching under long-term test conditions in the polyol aqueous-phase oxidation system.

To further rationalize the excellent catalytic performance of the Pt₁/HAP catalyst for the selective oxidation of low carbon polyols, DFT calculation, kinetic isotope effect (KIE) measurements, in-situ FT-IR and reaction kinetics were performed (Table S11, Table S12, Figure 4-5 and Figure S10-S16). Potential active sites for exploring the reaction mechanism were considered. Firstly, the active site formed by atomically dispersed Pt and O (belonging to PO₄³⁻ ligand) is defined as Pt₁-OPO₄³⁻ switch (Figure 4a). The concept of switch in Pt₁-OPO₄³⁻ originates from the Pt-(O-P) linkage cyclic catalysis that partial bonding states between Pt₁ and five O atoms could continuously break and regenerate during the oxidation reaction due to the stable tetrahedral characteristics of PO₄³⁻ ligand (Figure S10a). On this basis, surface

O* from O₂ direct dissociation and OH* from water assisted O₂ activation (all derived from Pt₁-OPO₄³⁻ switch) could generate Pt₁-O* and Pt₁-OH* active sites. Subsequently, four types of reaction pathways, defined based on the active sites involved such as Pt₁-O* assisted pathway I, Pt₁-OH* assisted pathway II, Pt₁-OPO₄³⁻ switch assisted pathway III and coupled Pt₁-OH*/Pt₁-OPO₄³⁻ switch assisted pathways IV were explored to reveal the formation of glyceric acid. As shown in Figure 4(b-1), three successive steps of glycerol activation namely dehydrogenation of O-H and C-H bonds as well as OH oxidation are involved. Obviously, pathway IV promoted by Pt₁-OH*/Pt₁-OPO₄³⁻ switch is much more energetically

favorable than that of pathway I, II or III. In this optimal pathway IV, the H₂O assisted O₂ activation exhibits lower transition state free energy than the direct O₂ dissociative adsorption, inducing the formation of Pt₁-OH* instead of Pt₁-O* participating in the oxidation reaction. Subsequently, Pt₁-OPO₄³⁻ switch and Pt₁-OH* are responsible for the activation of C-H and O-H bonds respectively, promoting the oxidation of glycerol to glyceric acid.

Notably, C-H bond activation in oxygen-containing intermediate (especially RCH₂O* intermediate) with the highest free energy is the rate determining step (RDS) in each oxidation reaction pathways. Among the active sites tested, the Pt₁-OPO₄³⁻ switch significantly reduces the transition state free energy of C-H bond activation in RDS. To further verify the reliability of the RDS obtained by DFT calculation, KIE experiment was performed to study the C-H bond cleavage rate by investigating the initial reaction rates in the solution of H₂O/D₂O and CH₂OHCHOHCH₂OH (glycerol) /CD₂OHCD₂OH (deuterated glycerol). Figure 4c shows that a small KIE value of 1.03 is obtained by adjusting H₂O/D₂O, suggesting that the isotopically substituted atom broken in the reactant is the non-kinetic relevant step.⁵⁴ In sharp contrast, a high KIE value ($K_H/K_D = 2.70$) for an exchange of glycerol to deuterated glycerol is obtained. It strongly proves that the activation of C-H bond of glycerol is the RDS, which fully supports the results from DFT calculations. Further analysis on reaction configurations and Mulliken charge in RDS (Figure S10) shows that the Pt-(O-P) linkage in Pt₁-OPO₄³⁻ switch plays a vital role in the activation of C-H bond. When the oxygenated substrate (O-R) is adsorbed on Pt₁-OPO₄³⁻ switch, previous bottom Pt-(O-P) linkage breaks with the formation of new top Pt-(O-R) linkage (switching on). Transition state (TS2) in RDS clearly shows that atomically dispersed Pt atom preferentially bonds to O in the primary OH group of the oxygenated intermediate, while the OPO₄³⁻ in the Pt₁-OPO₄³⁻ switch tends to remove the H of C-H bond. Meanwhile, there is an obvious electron transfer between oxygenated intermediate and Pt₁-OPO₄³⁻ switch. C-H bond is acidic (positively charged) and OPO₄³⁻ is basic (negatively charged). The basic OPO₄³⁻ attacks the acidic C-H band leading to an attraction of H. Essentially, the strong interaction between atomically dispersed Pt and PO₄³⁻ ligand triggers partial negatively charged O, thus significantly reconstructing the electronic local environment of Pt₁-OPO₄³⁻ switch. Due to this synergistic effect, Pt₁-OPO₄³⁻ switch is endowed with the dehydrogenation activity for the C-H bond activation (similar to oxidative dehydrogenation). With the desorption of product, top Pt-(O-R) linkage is broken and bottom Pt-(O-P) linkage is re-bonded (switching off), thus realizing the Pt-(O-P) linkage cyclic catalysis of Pt₁-OPO₄³⁻ switch (Figure S10a).

In addition, compared to the glycerol oxidation to dihydroxyacetone, the glycerol oxidation to glyceric acid is energetically preferred over Pt₁/HAP (001) because of its lower transition state free energy (Figure 4(b-2)). Glycerol tends to oxidize primary hydroxyl rather than secondary hydroxyl to produce glyceric acid over Pt₁/HAP. Furthermore, free energy diagram for the oxidation of glyceric acid shows that the existence of Pt₁-OPO₄³⁻ switch greatly inhibits the occurrence of deep oxidation reaction, especially the C-C bond

cleavage (Figure S12). Compared to the Pt (111) model, the atomically dispersed Pt with partial positively charge could supply much fewer electrons for the formation of Pt-C bond during the cleavage of C-C bond due to the lack of Pt-Pt active sites (Figure S11), hence weakening the back-donating interaction between Pt and glyceric acid. In other words, the presence of strong PO_4^{3-} -coordination effect in Pt_1/HAP induces the formation of deficient electron state of Pt_1 . This Pt_1 repulses the adsorbed C-C bond from $\text{Pt}_1\text{-OPO}_4^{3-}$ switch, suppressing the C-C bond cleavage and leading to the significant improvement of hydroxyl acid product selectivity compared with Pt/AC. This is in good agreement with the experimental observation (Table S6-10).

In-situ FT-IR of glycerol oxidation over Pt_1/HAP further confirmed the above conclusions of DFT calculation. Figure 5a shows that the peak of the intermolecular hydrogen bonds of glycerol in the $1660\text{-}1640\text{ cm}^{-1}$ gradually disappears with the increase of temperature, and the peak of C=O bond is dominant at high temperature ($\geq 80^\circ\text{C}$), proving that glycerol converts into carboxylic acid products.⁵⁵ Meanwhile, the νCO region in Figure 5b shows that the characteristic peaks of α interaction in the $1125\text{-}1075\text{ cm}^{-1}$ (belonging to alkoxy bond from primary hydroxyl and active sites) and γ interaction in the $1075\text{-}1000\text{ cm}^{-1}$ (belonging to primary hydroxyl) shift to the high wavelength with the increase of temperature, indicating the activation of primary hydroxyl group of glycerol.⁵⁵ In contrast, the position of the characteristic peak of β interaction in the $1200\text{-}1125\text{ cm}^{-1}$ (belonging to the activation of secondary hydroxyl) remains unchanged. This further confirms that glycerol is mainly oxidized to glyceric acid via the activation of primary hydroxyl rather than secondary hydroxyl on Pt_1/HAP (Figure 5c), which is consistent with the results of DFT calculation. In addition, the in-situ FT-IR results of glycerol conversion on Pt/AC are similar to those on Pt_1/HAP (Figure S13), indicating that Pt-Pt and $\text{Pt}_1\text{-OPO}_4^{3-}$ switch active sites have the same glycerol acid generation pathway.

Kinetic study of glycerol selective oxidation was further carried out on Pt/AC and Pt_1/HAP at different temperatures. The reaction rates of Reaction 1-3 were estimated based on the formation rate of each compound (supplementary information 2.11). The Arrhenius plots for the Reaction 1-3 were presented in Figure S15. The activation energies and pre-exponential factors estimated based on the reaction rate as well as the TOF for Pt/AC and Pt_1/HAP were summarized in Table S12. The apparent entropy changes (ΔS) were estimated from the pre-exponential factors based on the transition state theory (Table S12). The apparent entropy change reflects the freedom loss of the transition states of the rate determining step of each reaction compared to the reactants caused by the adsorption on the surface.⁵⁶ Larger ΔS (absolute value) represents the stronger the bound state of adsorbed intermediate over the active center.⁵⁷ Table S12 shows that Pt/AC and Pt_1/HAP exhibit similar ΔS ($\sim -148\text{ kJ/mol}$) for glycerol to glyceric acid (Reaction 1), suggesting that the adsorption strength of glycerol on $\text{Pt}_1\text{-OPO}_4^{3-}$ switch active site is close to that of Pt-Pt active site. It resulted in a similar activation energy. In addition, the estimated apparent activation energy (E_a) for the oxidation of glycerol to glyceric acid over Pt_1/HAP ($E_{a1} = 34.5\text{ kJ/mol}$) and Pt/AC ($E_{a1} = 34.9\text{ kJ/mol}$) is well consistent with that estimated apparent activation energy based on the Gibbs free energy profiles using the DFT calculation results (Figure S16). In a sharp

contrast, the apparent ΔS of glycerol to glycolic acid and formic acid involving a C-C bond cleavage (Reaction 2) is significantly lower on Pt₁/HAP (-35.8 kJ/mol) than that on Pt/AC (-122.6 kJ/mol), while the E_a is just the opposite. It means that the atomically dispersed Pt on HAP significantly destabilizes the transition state from glyceric acid toward C-C cleavage reaction, resulted in a significantly high activation energy. Combining the lower desorption energy of glyceric acid and higher activation energy of its conversion, a higher selectivity of glyceric acid is obtained. Consequently, reaction kinetics and DFT calculation fully indicate that the Pt₁-OPO₄³⁻ switch active site in Pt₁/HAP not only displays similar catalytic activity to Pt-Pt active site in Pt/AC (for C-H activation), but also shows excellent selectivity for hydroxyl acid products via inhibiting the cleavage of C-C bond. This approach introduced in this contribution could effectively bridge the relationship between the microstructure of Pt₁/HAP and the catalytic performance of low-carbon polyol oxidation to hydroxyl acid.

In summary, a novel in-situ synthesis method is established to stabilize isolated Pt atom on the HAP support. Significantly, this Pt₁/HAP catalyst is efficient for the selective oxidation of low carbon polyols with excellent hydroxyl acids selectivity and catalyst stability. Multi-characterizations together with detailed kinetic study and DFT calculation demonstrated that partial negatively charged PO₄³⁻ stably coordinates the atomically dispersed Pt atom, leading to an excellent resistance against leaching. Furthermore, the strong PO₄³⁻-coordination effect of Pt₁/HAP constructs the switchable Pt-(O-P) linkage, i.e., Pt₁-OPO₄³⁻ active site. Due to this electronic coupled Pt₁-OPO₄³⁻ switch, the activation of C-H bond of the key oxygen-containing intermediate is promoted and the C-C bond cleavage of hydroxy acid product is well suppressed in the oxidation process. This work opens a new paradigm of rational design of atomically dispersed leaching free catalysts in production of fine chemicals, pharmaceutical intermediates, as well as in catalytic biomass conversion processes.

Declarations

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Conflict of Interest

The authors declare no conflict of interest.

Author contributions

Hao Yan: Conceptualization, Methodology, Investigation, Writing - original draft. **Mingyue Zhao:** Investigation. **Xin Zhou:** Investigation. **Siming Zhao:** Conceptualization. **Shangfeng Li:** Visualization. **Minghao Zha:** Supervision, Funding acquisition. **Xiang Feng:** Project administration Validation, Writing -

review & editing. **Xiaobo Chen**: Investigation. **Yibin Liu**: Writing - review & editing. **De Chen**: Writing - review & editing. **Ning Yan**: Formal analysis. **Chaohe Yang**: Supervision, Funding acquisition, Validation.

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Figures

Figure 1

a) Synthesis, b) EDX mapping images (O violet, P dark green, Ca green and Pt blue) and c) aberration-corrected HAADF-STEM of the Pt₁/HAP catalyst.

Figure 2

a) The k^3 -weighted Fourier transform spectra derived from EXAFS. b) Schematic illustration of isolated Pt atom located on the surface of HAP. c) WT-EXAFS of the Pt L-edge signal of the Pt foil, PtO_2 and Pt_1/HAP catalyst. d) Normalized XANES spectra at the Pt L3-edge for the Pt_1/HAP catalyst. e) Chemisorption/reduction of different probe molecules for the Pt/AC, Pt_1/HAP and HAP samples: e-1) H_2 -

TPR, e-2) NH₃-TPD and e-3) CO₂-TPD profiles. f) DRIFTS spectra of CO adsorption for the f-1) Pt/AC and f-2) Pt₁/HAP catalysts. g) CO-TPD profiles for the AC, HAP, Pt/AC and Pt₁/HAP samples.

Figure 3

a) Schematic illustration for the conversion of low carbon polyols to primary carboxylic acid. b) Conversion, selectivity of various hydroxyl acids and initial reaction rate for the oxidation of b-1) glycerol [0.7 g HAP/ Pt₁/HAP or 0.2 g Pt/AC, 25 mL aqueous phase solution (0.05 M), 0.5 g NaOH, 50°C, 1MPa

O₂, 16 h], b-2) ethylene glycol [0.25 g HAP/ Pt1/HAP or 0.1 g Pt/AC, 25 mL aqueous phase solution (0.05 M), 0.5 g NaOH, 60°C, 1MPa O₂, 16 h], b-3) 1,2-propylene glycol [0.25 g HAP/ Pt1/HAP or 0.1 g Pt/AC, 25 mL aqueous phase solution (0.05 M), 0.5 g NaOH, 160°C, 1MPa O₂, 16 h] and b-4) 1,2-butanediol [0.7 g HAP/ Pt1/HAP or 0.2 g Pt/AC, 25 mL aqueous phase solution (0.05 M), 0.5 g NaOH, 140°C, 1MPa O₂, 16 h]. c) Catalytic stability of Pt/AC and Pt1/HAP catalysts. A deactivation factor of φ has been defined as $\varphi = X_n/X_0$, where X_n and X_0 are the conversion at the cycle of n and 0, respectively, which can be obtained by extrapolation to recycle number of 0. The closer φ is to 1, the slower deactivation is indicated.

Figure 4

a) Potential active sites originates from switchable Pt-(O-P) linkage. b) Free energy diagrams for the oxidation of glycerol (GLY) to b-1) glyceric acid (GLYA) and b-2) dihydroxyacetone (DHA) over Pt1/HAP (001) model at 298K. c) Glycerol (CH₂OHCHOHCH₂OH) and deuterated glycerol (CD₂OHCD₂OH) conversion as a function of time over Pt1/HAP catalysts in H₂O and D₂O.

Figure 5

In-situ FT-IR spectra of glycerol oxidation over Pt1/HAP at (a) carbonyl region (1500-1900 cm⁻¹) and (b) vCO region (1000-1200 cm⁻¹). (c) Summary schematic of the selective oxidation of glycerol to glyceric acid.

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