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Article

Site-specific deposition creates electron-rich Pd atoms for unprecedented C–H activation in aerobic alcohol oxidation

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ABSTRACT

Here, we demonstrate a photochemical strategy to site-specifically deposit Pd atoms on Au nanoparticles. The high-sensitivity low-energy ion scattering spectra combined with the X-ray photoelectron spectra reveal that the surface electronic structure of Pd can be continuously regulated by tailoring the Pd-to-Au molar ratio and the location of Pd atoms in AuPd nanoparticles. It is revealed that electron-rich Pd atoms are considerably more active than the net Pd atoms in aerobic alcohol oxidation. Remarkably, the catalyst with the most electron-rich Pd sites (binding energy downshift: 1.0 eV) exhibits an extremely high turnover frequency (~500000 h⁻¹ vs 12000 h⁻¹ for that with net Pd atoms) for solvent-free selective oxidation of benzyl alcohol, which is, to the best of our knowledge, the highest value ever reported. Kinetic studies reveal that electron-rich Pd atoms can accelerate the oxidation of benzyl alcohol by facilitating C–H cleavage, as indicated by the significant reduction in the activation energy as compared to net Pd atoms.

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1. Introduction

C–H activation is a key step in organic transformations and is considered very useful in petrochemical, pharmaceutical, and fine chemical industries [1–4]. However, due to the high bond energies of C–H bonds, the catalytic and selective activation of C–H bonds (particularly in alkanes) to produce high value-added compounds is a significant challenge [5]. The key to solve this problem lies in the successful development of efficient catalysts and the comprehensive understanding of the reaction mechanism.

Among the various transition metals, Pd has long been recognized as an efficient component to activate C–H bonds in alkanes [6–8], alcohols [9–14], and aromatic compounds [3,15,16]. During the last few years, several efficient Pd catalysts including single-site Pd catalysts [17] and Pd-based bimetallic nanocatalysts [18–22] have been developed to maximize the utilization of Pd. In particular, researchers have systematically investigated the catalytic performances of AuPd nanomaterials toward C–H activation of alcohols [10], toluene [15], and more recently, methane [7]. They have proposed that Au can electronically influence the catalytic properties of Pd. Be-

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sides, the low-coordination number corner and edge positions are implicated as active sites for C–H activation. It is clear that the microstructure and electronic structure of Pd sites are crucial to the realization of C–H activation [23,24]. However, due to the lack of an in-depth understanding of the relationship among Pd location, electronic structure, and catalytic performance, the rational control of the electronic structure of Pd in bimetallic nanocrystals to regulate the catalytic performance is considered highly challenging. The key challenges include: (1) site-specific deposition of Pd atoms on metal nanocrystals, (2) continuous regulation of the surface electronic structure of Pd, and (3) precise determination of the location and electronic structure of Pd at low Pd contents.

Here, we report a systematic study of AuPd bimetallic catalysts performed with the aim of addressing each of the above issues. First, using the high-sensitivity low-energy ion scattering technique to precisely determine the surface Pd-to-Au atomic ratio, we prove that stepwise photodeposition enables site-specific deposition of Pd atoms on Au nanoparticles (NPs). The control of Pd location on Au NPs enables the continuous regulation of the surface electronic structure, which provides an ideal model for the study of the structure-property relationship. Moreover, it is revealed that electron-rich Pd atoms promote C–H activation, thereby significantly reducing the activation energy of benzyl alcohol oxidation. A maximum turnover frequency (TOF; $\sim 500000 \text{ h}^{-1}$) is achieved by the synthesized AuPd/TiO₂ catalyst whose Pd 3d X-ray photoelectron spectroscopy (XPS) peak downshifts by 1.0 eV as compared to net Pd atoms.

2. Experimental

2.1. Synthesis of AuPd_x/TiO₂ catalysts

AuPd_x/TiO₂ catalysts were synthesized by a stepwise photodeposition method, with a fixed Au loading of 1 wt% [25,26]. Typically, 10 mmol L⁻¹ HAuCl₄ (0.51 mL) and TiO₂ (100 mg) were dispersed in 10 mL of methanol solution in a Pyrex quartz reactor. Before the irradiation process, gaseous Ar was bubbled through the mixture for 30 min to ensure that the solution had no dissolved O₂. The mixture was then subjected to UV light irradiation for 1 h using a high-pressure Xe lamp (300 W) as the light source. During the photodeposition process, the color of the mixture gradually changed, indicating the reduction of the metal precursors. Subsequently, a certain amount (depending on the Pd-to-Au ratio) of 10 mmol L⁻¹ H₂PdCl₄ was added into the mixture, and the resulting mixture was irradiated for 1 h to obtain AuPd_x/TiO₂. The resulting powder was collected by centrifugation, washed twice with ethanol, and then dried at room temperature in a vacuum oven. Au/TiO₂ and Pd/TiO₂ samples were synthesized by similar procedures.

2.2. Catalytic measurements

The oxidation of benzyl alcohol was conducted in a stirred autoclave reactor (30 mL, DHA-M630, China). The reaction condition including oxygen pressure was optimized before the

systematic investigation of the synthesized AuPd_x catalysts. Typically, the vessel was first charged with alcohol (4 mL) and the catalyst (10 mg). The autoclave was then purged three times, with oxygen leaving the vessel at 1.0 MPa gauge. Subsequently, the reaction mixture was placed in the heating system for 20 min for the temperature to reach the required value and stirred at 700 rpm. An oxygen cylinder was connected to maintain the pressure. The products were collected and analyzed by gas chromatography mass spectrometry and gas chromatography with a flame ionization detector. The products were identified by comparing with known standards. To quantify the amounts of reactants consumed and products generated, the external calibration method was used.

2.3. Characterization

Transmission electron microscopy (TEM) images were recorded using a Hitachi HT7700 microscope operated at 120 kV after drop casting the nanocrystal dispersions onto carbon-coated Cu grids and drying under ambient conditions. High-resolution TEM (HR-TEM) images, and elemental mapping and line-scanning profiles were obtained using a JEOL JEM2100F electron microscope. Powder X-ray diffraction patterns were recorded on a Rigaku Ultima IV diffractometer with the Cu KR radiation. The metal contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo iCAP6300). The high-sensitivity low-energy ion scattering (HS-LEIS) spectra were obtained using an Ion-TOF Qtac100 instrument. To minimize the surface damage, a neon ion source was used; the kinetic energy was 3 keV, ion flux was 6000 pA m⁻², and spot size was 2 mm × 2 mm.

3. Results and discussion

AuPd_x/TiO₂ (*x* is the Pd-to-Au molar ratio; Au mass loading was fixed at 1 wt% for all samples) catalysts were synthesized by a stepwise photodeposition method [25,26], as schematically illustrated in Fig. 1. Firstly, AuCl₄⁻ ions were reduced to Au NPs on TiO₂ by the photogenerated electrons. Owing to the high work function, the as-obtained Au NPs serve as a sink of photoinduced electrons, which subsequently reduce the Pd²⁺ ions on the surface of Au NPs, yielding Au@Pd core-shell structures [18]. According to the literature [27], the hot electrons generated when Au/TiO₂ is subjected to UV irradiation concentrate along the corners and edges of the Au NPs. Accordingly, photodeposition of Pd initially takes place at the corners and edges of Au NPs, and then, on the terraces, forming mono- and multilayers. The location of Pd on Au NPs can therefore be controlled by tuning the Pd-to-Au feeding ratio. The ICP-OES results (Table S1) suggest that the actual loading and Pd-to-Au ratio is accordant with normal value.

For AuPd_x/TiO₂ catalysts with large Pd-to-Au ratios, the Au@Pd core-shell structure could be determined by TEM. Figure 2a shows a typical TEM image of AuPd_{1.0}/TiO₂. Clearly, the AuPd NPs have a spherical morphology and sizes of around 8 nm. As observed from the line-scanning profile of a representative particle (Fig. 2b), strong Au and Pd signals are detected

Fig. 1. Schematic illustration of $\text{AuPd}_x/\text{TiO}_2$ catalyst synthesis. A mixture of HAuCl_4 methanol solution and TiO_2 was irradiated with a Xe lamp (300 W) for 1 h before the introduction of PdCl_2 . After UV irradiation for 1 h, the resulting $\text{AuPd}_x/\text{TiO}_2$ catalyst was collected and thoroughly washed with water. The location of Pd on the Au NPs was governed by the Pd-to-Au molar ratio.

from the particle center and particle edges, respectively. The elemental mapping images reveal that the diameter of Au distribution is smaller than that of Pd distribution (Fig. 2c). These results clearly indicate that the photodeposited AuPd_x particles have typical $\text{Au}@\text{Pd}$ core-shell structures. Besides, the AuPd/TiO_2 and Au/TiO_2 samples exhibit similar $\text{Au}(200)$ diffraction peaks without visible shifts (Fig. S1), further confirming the formation of a core-shell structure rather than an alloy.

For $\text{AuPd}_x/\text{TiO}_2$ catalysts with low Pd contents, because the contrast between Pd and Au was poor, it was difficult to identify the exact location of Pd atoms in the AuPd NPs by traditional approaches including elemental mapping and line-scanning analysis. To address this problem, HS-LEIS, a technique with surface sensitivity and specificity usually used to analyze the outermost atomic layer [28,29], was employed to determine the surface composition of the photodeposited AuPd_x samples. As shown in Fig. 3a, a variation in the Pd-to-Au ratio leads to changes in the relative intensities of Pd and Au. The surface atomic ratios of Pd were quantitatively analyzed from the Pd-to-Au relative intensity ratio determined by HS-LEIS. For comparison, the theoretical values were calculated by

site-specific deposition of Pd on icosahedral Au (~ 8 nm). Pd atoms were assumed to deposit first on the corners and edges of Au NPs, and then, on the terraces, forming mono- and multi-layers. Specifically, a monolayer coverage of Pd on icosahedral Au requires a minimal Pd-to-Au surface ratio of 0.20, while the occupation of all the corners and edges of icosahedral Au by Pd atoms requires a minimal surface Pd-to-Au ratio of 0.001 and 0.05, respectively (see the Supporting Information for details). It is interesting to note that the experimental results roughly fit the theoretical results (Fig. 3b), suggesting that the photodeposition of AuPd proceeded as expected. For a Pd-to-Au ratio lower than 0.2 (red region), the $\text{Pd}/(\text{Au} + \text{Pd})$ surface atomic ratio linearly increases with the Pd-to-Au ratio, corresponding to the process of Pd monolayer formation on Au [30]. Once Au NPs are fully covered by Pd, a further increase in the Pd-to-Au ratio hardly influences the $\text{Pd}/(\text{Au} + \text{Pd})$ atomic ratio on the outmost surface.

The electronic structures of photodeposited AuPd_x were investigated by XPS. Due to the overlap of $\text{Pd } 3d_{5/2}$ and $\text{Au } 4d_{5/2}$ peaks, $\text{Pd } 3d_{3/2}$ (Fig. 3c and S2) and $\text{Au } 4f_{7/2}$ peaks (Fig. S3) were used to analyze the electronic structures of Pd and Au, respectively. The constant Ti and O XPS signals (Fig. S4) indicate that the electronic structure of the TiO_2 support is barely affected by the deposited AuPd particles. Interestingly, as the Pd-to-Au ratio decreases from 1.0 to 0.006, the $\text{Au } 4f_{7/2}$ peaks slightly upshift to higher binding energies, while the $\text{Pd } 3d_{5/2}$ peaks downshift to lower binding energies (Fig. 3d). The opposite trends suggest that electrons are transferred from Au to Pd. As compared to those in the Pd monometallic catalyst, Pd atoms in the photodeposited AuPd catalysts are electron rich (denoted as $\text{Pd}^{\delta-}$). Besides, no visible Pd^{2+} peaks are detected in samples with Pd-to-Au ratios below 0.2. Similar results have been reported in the literature [31,32]. A sharp change in the $\text{Pd}^{\delta-}$ binding energy is observed during Pd monolayer formation (Pd-to-Au ratio less than 0.2), suggesting a significant variation of the electronic structure of the Pd atom (Fig. 3d). A charge compensation model in which Au donates d electrons to Pd and accepts sp electrons was proposed to interpret the interaction between Au and Pd [31,32].

More importantly, the variation of $\text{Pd } 3d_{5/2}$ and $\text{Au } 4f_{7/2}$ peak positions with the Pd-to-Au ratio implies that the electronic structure of Pd atoms in AuPd_x can be regulated by changing the Pd atomic locations. Pd atoms located at the corners of $\text{AuPd}_{0.006}$ are the most electron rich, featuring a 1.0 eV down-

Fig. 2. TEM analysis of $\text{AuPd}_{1.0}/\text{TiO}_2$ catalyst. (a) TEM image; (b) Line-scanning profile; (c) Elemental mapping images.

Fig. 3. Characterization of AuPd_x/TiO₂ catalysts. (a) HS-LEIS spectra for photodeposited AuPd_x catalysts; (b) Pd/(Au + Pd) surface atomic ratios calculated from the HS-LEIS data and the theoretical values; (c) Pd 3d XPS profiles for photodeposited AuPd_x catalysts; (d) Pd^{δ-} XPS peak positions for AuPd_x catalysts.

shift in the binding energy as compared to that of the net Pd. Pd atoms in the Pd mono- and multilayers are less electron rich, resembling those of monometallic Pd catalysts. Interestingly, once AuPd_{0.05} is calcined at 350 °C (denoted as AuPd_{0.05}-calcined), Pd atoms tend to diffuse into the bulk of Au NPs or aggregate into large particles. Subsequently, the Pd/(Pd + Au) surface atomic ratio declines from 0.23 to 0.01 (Fig. 3b). The rearrangement of the surface Au and Pd atoms eventually changes the electron-rich structure of Pd atoms (Fig. S5).

Figure 4a shows the relationship between Pd-to-Au ratios and TOF values of AuPd catalysts for solvent-free oxidation of benzyl alcohol; the structural models of the catalysts are also shown. The number of Pd atoms needed for covering the corners, edges, and facets are calculated using an icosahedral model (see the Supporting Information for details); the corresponding conversion and selectivity data for benzyl alcohol oxidation over AuPd_x are listed in Table S2. Basically, all AuPd_x catalysts show good selectivity toward benzaldehyde (>80%).

The main by-products include toluene, benzoic acid, and benzyl benzoate. Interestingly, Au/TiO₂ hardly shows any activity for benzyl alcohol oxidation at the given reaction conditions, excluding Au atoms as the active sites. Similar results have been reported in the literature [41]. Accordingly, we considered only the surface Pd atoms as the active sites and defined the TOF value as the number of benzyl alcohol molecules reacted per hour per surface Pd atom. It is important to highlight that AuPd_{0.001} exhibits the maximum TOF of ~500000 h⁻¹, which is, to the best of our knowledge, the highest value ever reported for solvent-free oxidation of benzyl alcohol at similar reaction conditions (Table 1). As the Pd-to-Au ratio increases to 0.03 and 0.05, Pd atoms begin to deposit on the edges of Au NPs and become less electron rich. As a result, the TOF declines to ~200000 h⁻¹. By plotting the TOF as a function of the Pd binding energy (Fig. 4b), we can see that the TOF decreases almost linearly as the binding energy increases from 339 eV (AuPd_{0.006}) to 339.7 eV (AuPd_{0.2}). These results clearly demon-

Fig. 4. (a) Catalytic performance of photodeposited AuPd_x catalysts for benzyl alcohol oxidation. Reaction conditions: 10 mg of catalyst, 4.0 mL of benzyl alcohol, $P_{\text{O}_2} = 1.0$ MPa, and $T = 120$ °C. (b) TOF as a function of binding energy of $\text{Pd}^{\delta-}$. (c) Arrhenius plots of various AuPd_x catalysts for benzyl alcohol oxidation. (d) Catalytic performance of $\text{AuPd}_{0.05}$ for oxidation of various substituted benzyl alcohols. TOF values are defined as benzyl alcohol reacted per hour per surface Pd atom.

strate that electron-rich Pd atoms are more active in benzyl alcohol oxidation. As the Pd-to-Au ratio further increases, forming Pd monolayer and multilayers, the electron density of Pd decreases and approaches that of bulk Pd. Correspondingly, the TOF of AuPd declines, and finally, becomes the same as that of Pd.

To clearly elucidate the mechanism behind the electronic structure dependence, kinetic studies were conducted. As shown in Fig. 4c, the activation energy (E_a) of AuPd catalysts decreases from 127.0 kJ mol^{-1} for $\text{AuPd}_{0.60}$ to 30.5 kJ mol^{-1} for $\text{AuPd}_{0.006}$, indicating that electron-rich Pd atoms significantly reduce the activation energy of the reaction, accelerating the reaction. It is generally accepted that C–H and O–H cleavage are the key steps in alcohol oxidation [42–44]. To examine the reaction rate-determining step, kinetic isotope effect (KIE) was investigated using benzyl- d_2 alcohol ($\text{C}_6\text{H}_5\text{CD}_2\text{OH}$) and benzyl aldehyde-OD ($\text{C}_6\text{H}_5\text{CH}_2\text{OD}$) as substrates over $\text{AuPd}_{0.05}$ [45]. As

shown in Fig. 4d, a significant KIE ($k_H/k_D = 11.34$) is observed for benzyl- d_2 alcohol; however, the replacement of benzyl alcohol by benzyl aldehyde-OD barely changes the TOF ($k_H/k_D = 1.11$). These results indicate that the cleavage of C–H instead of O–H is the rate-determining step for benzyl alcohol oxidation over AuPd catalysts. Moreover, we investigated the substituent effect with 4-methoxybenzyl alcohol and 4-nitrobenzyl alcohol as reactants [44]. As shown in Fig. 4d, the presence of the methoxy group (electron-donating group) at 4-position remarkably increases the reaction rate, while the 4-nitro group (electron-withdrawing group) decreases the reaction rate. These results suggest that a rich electronic environment is crucial for C–H activation in aerobic alcohol oxidation [46,47]. It is interesting to note that after the calcination of $\text{AuPd}_{0.05}$ at 350 °C to demolish the electron-rich Pd atoms (Fig. S5), the TOF rapidly decreases from 212000 to 5100 h^{-1} . Combining all these results together, we can conclude that electron-rich Pd at-

Table 1

TOF of aerobic oxidation of benzyl alcohol over different catalysts.

Catalyst	<i>T</i> /°C	Pressure/MPa	Solvent	TOF ^a /h ⁻¹	Ref.
Au/CeO ₂	100	0.2	None	151 ^b	[33]
Pd/C	90	0.1	Trifluorotoluene	684	[34]
Pd/SiO ₂ -Al ₂ O ₃	80	Flowing	None	9000	[35]
Ni/PdH _{0.43}	100	0.2	None	2664	[36]
Au-Pd/TiO ₂	80	0.1	None	11520	[37]
0.73%Au-0.27%Pd/C	60	0.15	Water	593	[38]
2.5%Au-2.5%Pd/TiO ₂	160	0.1	None	133000	[10]
Au ₁ -Pd ₁ /C	120	1.0	None	100000	[39]
Au ₁ -Pd ₃ /C	120	1.0	None	80000	[39]
Au-Pd/Ce-NR	120	0.2	None	71800	[40]
AuPd _{0.001}	120	1.0	None	480000	This work
AuPd _{0.05}	120	1.0	None	210000	This work
AuPd _{0.05}	80	0.1	None	23133	This work

^aTOF was recalculated on the basis of Pd atoms or active sites from the literature. ^bTOF was calculated on the basis of Au atoms.

oms improve the reaction rate by promoting the C–H bond activation, decreasing the activation energy.

4. Conclusions

In this study, we have systematically investigated the relationship among the Pd location, surface electronic structure, and catalytic performance. Electron-rich Pd atoms in AuPd bimetallic NPs are revealed to facilitate C–H bond activation. Considering the recent success of Au–Pd catalyst application in methane selective oxidation [48], electron-rich Pd atoms could be a future hot spot for alkane activation. Furthermore, designing relative position of two metals to control the active sites in catalyst shines a light on the development of high-activity and cost-effective noble metal catalysts.

Supporting Information

Chemicals, XRD patterns, additional XPS spectra. This material is available free of charge via the Internet.

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Graphical Abstract

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Site-specific deposition creates electron-rich Pd atoms for unprecedented C–H activation in aerobic alcohol oxidation

Yang Yan, Bin Ye, Mingshu Chen, Linfang Lu, Jian Yu, Yuheng Zhou, Yong Wang, Juanjuan Liu, Liping Xiao, Shihui Zou*, Jie Fan*
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Site-specific deposition enables the continuous regulation of the surface electronic structure of Pd atoms on Au nanoparticles. Electron-rich Pd atoms facilitate C–H cleavage, resulting in extremely high turnover frequency for solvent-free selective oxidation of benzyl alcohol.

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特定位点沉积富电子钯实现醇氧化中超高碳氢键活化

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摘要: C–H键活化是石油化工、制药及精细化学品工业中的一个关键步骤, 负载型Pd基催化剂因其优异的催化活性而在该反应中得到广泛应用. 在过去的研究中, 人们发现引入第二金属组分能够改变Pd的配位结构和电子结构, 进而影响其C–H键活化的催化性能. 但是由于缺乏对Pd空间位置、电子结构和催化活性之间关系的深入理解, 通过精确控制Pd电子结构来优化其催化活性这一设想仍难以实现. 主要的挑战在于: (1)在特定的位点上沉积Pd; (2)连续调控Pd的表面电子结构; (3)精确表征低含量Pd样品中Pd的位置和电子结构.

本文采用分步光沉积方法合成了AuPd_x/TiO₂催化剂. 该方法首先利用光生电子的还原作用将AuCl₄[−]还原成Au纳米颗粒沉积在载体TiO₂上. 由于Au具有高功函, 光生电子会富集在Au上, 因此在随后的Pd沉积过程中, Pd会优先沉积在Au表面

形成Au@Pd核壳结构。Au表面不同位置具有不同的电荷,因此通过调控Au/Pd比例可以实现在不同的Au表面位点上沉积Pd。借助高灵敏度低能离子散射(HS-LEIS)技术,我们精确表征了表面层的Au/Pd原子比例,并与理论模型进行对比,证明了分步光沉积方法可以实现在Au纳米颗粒表面特定位置沉积Pd。通过X射线光电子能谱(XPS)对Pd的表面电子结构进行表征,我们发现在AuPd/TiO₂催化剂中,电子倾向于从Au转移到Pd,且通过调控Pd在Au表面的位置,可以连续地调控Pd的表面电子结构。催化结果和反应动力学研究表明,富电子的Pd可以促进苯甲醇氧化中的C–H键活化,进而显著降低反应的活化能。当Pd/Au原子比为0.001时,Pd 3d XPS偏移了1.0 eV。这种富电子Pd原子的TOF值高达500000 h⁻¹,是同类研究中最高的。考虑到近来AuPd催化剂在甲烷选择性氧化反应中的应用,本文的研究成果还可能进一步拓展到烷烃活化反应。此外,通过调控双金属的相对位置来调控催化反应活性这一研究策略有助于高活性催化剂的开发以及贵金属的节约利用。

关键词: AuPd/TiO₂; 苯甲醇; 选择性氧化; 碳氢键活化; 电子结构

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