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Short communication

Modification of Au nanoparticles electronic state by MOFs defect engineering to realize highly active photocatalytic oxidative esterification of benzyl alcohol with methanol



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ABSTRACT

Defect modified UiO-66 supported Au nanoparticles exhibited excellent catalytic performance in the oxidative esterification of benzyl alcohol with methanol under mild conditions. The defects were generated by introducing HCl during the preparation procedure. The defects exposed the Lewis acid of coordinatively unsaturated metal sites, which is benefit for Au loading and changing Au nanoparticles (NPs) to a negative electron state. The negatively charged Au nanoparticle promoted the reaction by strong oxygen activation ability. The present study could help to unravel the synergistic effect of support and metal interaction and provides an efficient photocatalytic route for synthesis high-value esters in terms of sustainable chemistry.

1. Introduction

Esterification plays an important role in the fine chemical industry because the ester products are widely used in solvent, lubricating oil, medicine and essence. Compare to traditional synthetic paths that esterification of acid derivatives (acyl chlorides and anhydrides) with alcohols which require a stoichiometric amount of a toxic coupling agent, the tandem reaction to direct oxidative esterification of alcohol presents a significant advance in decreasing raw material cost, reducing energy consumption and improving atomic utilization [1]. Up to now, a variety of metal catalysts such as Pt, Pd and Co have been widely explored for direct oxidative esterification of alcohols, which realized catalytic transformation with oxygen as oxidant but require harsh condition (high temperature and hyperbaric oxygen) [1-3]. It is well known that Au NPs showed photo catalysis ability due to the localized surface plasmon resonance (LSPR) effects, which can absorb and utilize visible light to achieve esterification of alcohol under mild conditions [4,5]. Specially, the anionic of Au have a significant effect on oxygen activation, which plays an important role in enhancing the catalytic efficiency of aerobic oxidation [6-9]. It is well established that the defects in support can act as potential active sites to immobilize Au and change the electronic state of Au NPs [10]. Moreover, some materials with defects expose Lewis acidic sites, which can promote alcohol

adsorption and activation. Therefore, it is very attractive to promote catalytic ability by regulating defects of support to change the metal electronic state.

Porous materials have gained increasing attention in recent years [11,12], as a porous material with a large specific surface, metal-organic frameworks (MOFs) usually serve as carrier to introduce active catalytic components to form a host-guest structure [13,14]. Among which, UiO-66 shows an excellent acid/alkali and thermal stability [15]. The combination of metal nanoparticles with UiO-66 as heterogeneous catalyst has been widely studied in organic transformations [16–18]. Studies shown that introducing modulators during synthesis can produce missing linkers by competing with ligands, which exposes the Lewis acid of unsaturated coordination central metal clusters and enhanced the absorption of precious metal ions [17,19,20]. Therefore, we believe that it is feasible to introduce modulators in UiO-66 to fabricate material defects, so as to expose the Lewis acid and change the electronic state of Au NPs to improve the catalytic activity.

Herein, the defective UiO-66 was prepared by using HCl as a modulator, the Cl⁻ originated from HCl partially replaced the ligand to form ligand defects. It reduced steric hindrance and benefit for the adsorption of AuCl₄⁻, thereby uniformly Au NPs can be loaded on the UiO-66 by a photo-deposition method. The strong interaction between Au NPs and UiO-66 formed negatively charged Au NPs, which is

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Fig. 1. High-resolution Au 4f XPS spectra of Au/UiO-66 and Au/UiO-66-HCl.

favorable for activating O_2 in the reaction. The Lewis acid sites together with the negatively charged Au NPs realized efficient oxidative esterification of benzyl alcohol with methanol to methyl benzoate at room temperature and atmospheric pressure oxygen under visible light irradiation.

2. Experimental

UiO-66 was synthesized by a hydrothermal method [21], defective

UiO-66 (UiO-66-HCl) was synthesized by a modified procedure according literature using HCl as regulator [22], Au NPs were loaded on the support by photo-deposition method. The detailed catalysts synthetic methods, information about characterization instruments and catalysts performance evaluation for alcohols oxidative esterification reaction are presented in Supporting Information (SI⁺).

3. Results and discussion

3.1. Catalyst characterization

In the XRD pattern (Fig. S1), UiO-66 and defects contained UiO-66-HCl samples were completely consistent with the simulation value. indicated the HCl introduction cannot destroy the main skeleton structure of UiO-66. The thermogravimetric analysis (TGA), NH₃ temperature-programmed desorption (NH₃-TPD) and X-ray photoelectron spectroscopy (XPS) techniques were used to detected the defects. In TGA curves (Fig. S2), the weight loss curve can be divided into three stages: the dehydration and dehydroxylation process at 30-200 °C, the removal of the adsorption solvent and unbound BDC^{2-} molecules at 200-500 °C and the linker combust with collapse of framework above 500 °C. The last stage is usually used to compare the defect degree. UiO-66 exhibited more weight loss above 500 °C than UiO-66-HCl, indicating that HCl replaced the BDC²⁻ ligand to coordinate with metal cluster. NH₃-TPD is also a powerful characterization method to detect the defects of UiO-66, because the central metal clusters exhibited Lewis acidity to absorb NH₃ and the defects caused by changing the coordination ligand can affect the amount of the Lewis acid sites [23]. As shown in Fig. S3, the desorption peak at temperature around 100-250 °C of UiO-66-HCl increased to higher temperature, indicating the increased acid strength of UiO-66-HCl [24]. N2 adsorption-desorption isotherms (Fig. S4) exhibited an enhanced adsorption capacity

Table 1

Effect of various reaction conditions on the reactant conversion and product selectivity for the catalytic oxidative esterification of benzyl alcohol and methanol^a.



Entry	Catalyst	Base	Light	Con. ^b /%	Sel. ^b /%		
					В	С	D
1	Au/UiO-66	K ₂ CO ₃	Dark	0.4	99.9	0	0
2	Au/UiO-66	K ₂ CO ₃	Light	1.4	99.9	0	0
3	Au/UiO-66-HCl	K ₂ CO ₃	Dark	56.2	1.4	98.6	0
4	Au/UiO-66-HCl	K ₂ CO ₃	Light	94.3	0.7	99.2	0
5	UiO-66-HCl	-	Dark	0.4	99.9	0	0
6	UiO-66-HCl	-	Light	0.5	99.9	0	0
7	UiO-66-HCl	K ₂ CO ₃	Dark	0.9	99.9	0	0
8	UiO-66-HCl	K ₂ CO ₃	Light	1.8	99.9	0	0
9 ^c	Au/UiO-66-HCl	K ₂ CO ₃	Dark	0.9	99.9	0	0
10 ^c	Au/UiO-66-HCl	K ₂ CO ₃	Light	0.8	99.9	0	0
11	Au/UiO-66-HCl	-	Dark	0.6	99.9	0	0
12	Au/UiO-66-HCl	-	Light	0.8	99.9	0	0
13 ^d	Au/UiO-66-HCl	-	Dark	24.6	8.9	0	91.1
14 ^d	Au/UiO-66-HCl	-	Light	99.9	3.2	0	96.8

^a Reaction conditions: 1 mmol benzyl alcohol, 5 mL methanol, 10 mg catalyst, 0.25 mmol K_2CO_3 , 0.1 MPa O_2 , 30 °C, 1 h, white LED (477 nm) and light intensity 0.6 W cm⁻².

^b Conversion and selectivity were determined by gas chromatography (GC).

^c 0.1 MPa Ar.

^d 80 °C, 12 h.



Fig. 2. (a) AQE and UV/vis absorption of UiO-66-HCl and Au/UiO-66-HCl, (b) Effect of light intensity on catalytic activity of Au/UiO-66-HCl, (c) Superoxide radical capture experiment and (d) ESR spectra of radical adducts trapped by DMPO (DMPO- O_2^{-}). Reaction condition: 1 mmol benzyl alcohol, 5 mL methanol, 10 mg catalyst, 0.25 mmol K₂CO₃, 0.1 MPa O₂, 30 °C, 1 h.

for UiO-66-HCl with the HCl introduction, the Brunauer-Emmett-Teller (BET) surfaces area increased from 497.8 m^2g^{-1} of UiO-66 to 1170.2 m^2g^{-1} of UiO-66-HCl. The ligand deletion exposed unsaturated coordinated central metal clusters in the UiO-66-HCl, which significantly enhanced the specific surface area.

To further prove the replacement of BDC²⁻ ligand by Cl⁻, the XPS analysis was carried out. In the O 1 s spectra of UiO-66, three peaks at 530.10, 531.70 and 532.85 eV are assigned to oxygen atoms of the Zr–O, C=O and O–H bond, respectively (Fig. S5) [23,25]. After HCl was introduced in UiO-66-HCl, a new peak at 534.85 eV emerged, which can be identified as μ_2 -OH species. The binding energy of other three peaks shift to low binding energy. As a charge-balance anion, Cl⁻ bonded to metal cluster to maintain the neutrality of inorganic node where the ligand absence. For the structure of Cl⁻ is different from BDC²⁻, it coordinates with metal cluster will cause the arrangement of oxygen atoms that break a bond of μ_3 -OH to form μ_2 -OH, which gets close to the unsaturated coordinated metal cluster to stable the nodes [26]. All above results suggested the defects were introduced by HCl during the material preparation procedure.

The Au NPs were loaded on the UiO-66 and UiO-66-HCl via a photodeposition method. After Au NPs was loaded, no obvious variation can be observed in the XRD patterns of Au/UiO-66 and Au/UiO-66-HCl samples (Fig. S1). The Transmission Electron Microscopy (TEM) image showed the Au NPs of Au/UiO-66 are quite few (Fig. S6a), while the Au NPs were uniformly dispersed on Au/UiO-66-HCl (Fig. S6b). Besides, ICP results suggested the Au loading of Au/UiO-66-HCl (2.58 wt%) was higher than Au/UiO-66 (2.18 wt%) (Table S1).

After Au NPs were loaded, the relevant content of μ_2 -OH decreased from 25% in UiO-66-HCl to 9% in Au/UiO-66-HCl (Table S2). which indicated that ion exchange had occurred that AuCl₄⁻ replaced Cl⁻ to interact with μ_2 -OH. The same phenomenon also occurred in Zr 3d spectra (Fig. S5a). When one ligand is missing, the binding energy of Zr 3d will reduce because the decrease of O atoms from coordinated ligands. In the UiO-66-HCl, Cl⁻ replacement ligand bonded to the central metal cluster to maintain the charge balance. AuCl₄ $^-$ partially replaced Cl⁻ and were reduced to Au NPs during the photo-deposition process, which reduced the number of equilibrium charges and the binding energy of Zr 3d decreased from 182.35 eV of UiO-66-HCl to 182.25 eV of Au/UiO-66-HCl (Fig. S5a). The Au NPs connected with μ_2 -OH and underwent electron transport so as to increase the surface electron concentration of Au NPs. The result reflected in the binding energy of Au loaded on UiO-66-HCl (83.00 eV of Au $4f_{7/2}$) is much lower than the Au loaded at UiO-66 (83.70 eV of Au $4f_{7/2}$) (Fig. 1), which indicated the Au NPs in UiO-66-HCl were negatively charged [27-29].

3.2. Catalytic performance

The oxidative esterification of benzyl alcohol with methanol to methyl benzoate was used as the probe reaction to test the photocatalytic performance of all the above catalyst. Under room temperature and atmosphere oxygen, Au/UiO-66 exhibited no catalytic activity. While Au/UiO-66-HCl exhibited high catalytic performance with 94.3% conversion of benzyl alcohol and 99.2% selectivity to methyl benzoate. (Table 1, entries 1–4). The turn-over frequency (TOF) value of Au/UiO-



Fig. 3. Proposed reaction mechanism for Au/UiO-66-HCl oxidative esterification of benzyl alcohol and methanol to methyl benzoate.

66-HCl is 71 h⁻¹, which is higher than most of the Au based catalysts (Table S3). Moreover, Au/UiO-66-HCl exhibited good universality for various substitutions or aromatic alcohols (Table S4). There is no noticeable attenuation of the catalytic activity after five cycles, suggesting the high stability of Au/UiO-66-HCl under the applied reaction conditions (Fig. S7).

A series of control experiments were conducted to under the catalytic origin. No catalytic activity was observed when using UiO-66-HCl as catalyst with or without base and light irradiation (Table 1, entries 5–8), suggested the catalytic centers were Au NPs. No reaction occurred without O₂ (Table 1 entries 9–10), suggested the reaction is an aerobic oxidative process. The oxidative esterification reaction is inhabited in the absence of K_2CO_3 (Table 1, entries 11–12) even at high reaction temperature. The addition of alkali can significantly improve the catalytic efficiency by improving the efficiency of proton extraction in OH of benzyl alcohol to form benzyloxy [30]. Only by-product benzalde-hyde dimethylacetal can be obtained, which is catalyzed by the Lewis acid sites of defective UiO-66-HCl support (Table 1, entries 13–14), which is similar to AlCl₃ Lewis acid catalyst [31].

The conversion of benzyl alcohol increased from 56.2% in the dark to 94.3% under visible light irradiation, suggested the light adsorption of Au NPs via localized surface plasmon resonance (LSPR) effect play an important role in enhancing the catalytic activity. In the UV–vis spectrum, Au/UiO-66-HCl showed LSPR absorption peak at 520 nm (Fig. 2a). The impact of the irradiation wavelength on the catalytic activity was investigated, the apparent quantum efficiency (AQE) is calculated to eliminate the influence of thermal effect on photocatalytic performance. As shown in Fig. 2a, the AQE value closely matches the LSPR absorption spectrum of Au NPs and reaches the maximum at 522 nm, which indicates the photo-generated electron transfer is the driving force of the photocatalytic reaction.

The effect of the light intensity on the catalytic activity was investigated by varying the irradiance. As shown in Fig. 2b, the product yield obtained in the dark is considered as a thermal contribution and the increased yield under the visible light irradiation is considered as a light contribution [32]. With the light intensity increased from 0.1 to

0.6 W·cm⁻², the light contribution increased linearly. The result showed that a higher irradiance excites more energetic electrons on the Au surface and enhance the interaction with adsorbed molecules to improve the catalytic efficiency.

The activation of O₂ play an important role in the aerobic oxidative reaction, then EPR (Fig. 2d) was further conducted. The results indicated the reactive oxygen species is O_2 during the O_2 activation process. UiO-66 and UiO-66-HCl exhibited weak $\mathrm{O_2}^{-}$ signal, while the intensity of O₂[•] signal greatly enhanced when Au NPs were introduced. Moreover, Au/UiO-66-HCl shows better activation ability than Au/UiO-66. plays a major role in activation of O_2 . The product yield decreased gradually with the increase of O_2 capture agent content (Fig. 2c), which further proved the importance of O_2 in the aerobic oxidation reaction. Au/UiO-66-HCl exhibited higher TOF value than Au/UiO-66, which can be attributed to the greater surface electron concentrations of Au NPs and the higher O2 activation ability. It is well known the activation of O2 to O2 by Au NPs is sensitive to the negative charge state of Au [33,34]., the anionic Au NPs can activate O₂ by donating an excess electronic charge to the anti-bonding orbital of O2 to generate O₂, as the concentration of Au surface electrons increases, the oxygen activation ability increase [6,10,35].

To probe the effect of exposed Lewis acid sites in the oxidative esterification reaction, ethylenediamine was used to block the Lewis acid sites by grafting of amine groups from ethylenediamine onto coordinatively unsaturated Zr sites. As shown in Fig. S8, the conversion of benzyl alcohol decreased from 91.6% to 11.2% with the increase of ethylenediamine amount, which indicated the Lewis acid sites is benefit for the adsorption of reactants.

A possible mechanism was proposed (Fig. 3) based on the above analysis. Firstly, the defect sites in UiO-66-HCl were favorable for adsorption of the alcoholic hydroxyl groups of benzyl alcohol (I, II). Then the energetic electrons induced by LSPR effect of Au NPs were easily transferred to the LOMO orbital of O_2 and activated the O_2 to O_2^- . With the aid of alkali and O_2^- , benzyl alcohol undergoes cleavage of the alcoholic OH group on the Au surface to produce a benzyloxy, then cracked C–H to form benzaldehyde (III). The formed benzaldehyde condensed with methanol to form hemiacetal intermediate (V). Finally, methyl benzoate and H_2O are produced via the oxidative dehydrogenation of the hemiacetal intermediate (VI).

4. Conclusions

In summary, defective of UiO-66 was prepared by introducing HCl during the preparation procedure. The new coordination pattern reduced the attack steric hindrance of $AuCl_4^-$ and the defect sites served as an anchor to load Au NPs in the photo-deposition process. The strong interaction between Au NPs and defective UiO-66 support resulted negatively charged Au NPs, which is critical to activate O_2 in the aerobic oxidative reaction. Besides, the exposed coordinatively unsaturated Lewis acid sites are benefit for the adsorption of reactants. Thus Au/UiO-66-HCl exhibited high catalytic performance in the oxidative esterification of benzyl alcohol with methanol to methyl benzoate at room temperature under visible light irradiation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2020.106002.

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