Accepted Manuscript

Title: Aerobic oxidation of benzyl alcohol in water catalyzed by gold nanoparticles supported on imidazole containing crosslinked polymer





Please cite this article as: Huan Wang, Yuanyuan Shi, Masatake Haruta, Jiahui Huang, Aerobic oxidation of benzyl alcohol in water catalyzed by gold nanoparticles supported on imidazole containing crosslinked polymer, Applied Catalysis A, General http://dx.doi.org/10.1016/j.apcata.2017.02.015

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Aerobic oxidation of benzyl alcohol in water catalyzed by gold nanoparticles supported on imidazole containing crosslinked polymer

Huan Wang^{\dagger}, Yuanyuan Shi^{\dagger}, Masatake Haruta^{$*^{\dagger \ddagger}$}, and Jiahui Huang^{$*^{\dagger}$}

 [†]Gold Catalysis Research Center, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, P. R. China
 [‡]Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

Author Information

Corresponding author

*E-mail: jiahuihuang@dicp.ac.cn; haruta-masatake@center.tmu.ac.jp.

Graphical Abstract



Highlights

- A series of poly(divinylbenzene-*co-N*-vinylimidazole) (PDVB-VI-*n*) supported Au catalysts were prepared.
- Au/PDVB-VI-*n* exhibited the excellent activities even only using a small amount of basic K₂CO₃ after optimizing the sizes of Au NPs and the composition of PDVB-VI-*n*.
- The conversion of benzyl alcohol increased monotonously with the increase of Au sizes within the range of 2–5 nm, while the selectivity to benzoic acid increased first and then decreased gradually.
- Au NPs with the size of about 3.2 nm gave the highest selectivity to benzoic acid.

Abstract

A series of imidazole containing crosslinked copolymer poly(divinylbenzene-*co-N*-vinylimidazole) (PDVB-VI-*n*) supported Au catalysts were prepared by using AuCl₃ as the precursor. The resulting Au/PDVB-VI-*n* catalysts were employed to catalyze the aerobic oxidation of benzyl alcohol with molecular oxygen as the sole oxidant and water as the solvent. By optimizing the sizes of Au NPs and the composition of PDVB-VI-*n*, Au/PDVB-VI-*n* exhibited the excellent activities even only using a small amount of basic K₂CO₃. Interestingly, the conversion of benzyl alcohol increased monotonously with the increase of Au sizes in the range of 2–5 nm, but the selectivity to benzoic acid increased first and then decreased gradually. The highest selectivity to benzoic acid of ~80% was achieved over ~3.2 nm Au NPs.

Keywords: Gold catalysis • crosslinked polymer • aerobic oxidation • benzyl alcohol • benzoic acid

Introduction

Carboxylic acids, widely used as the intermediates for alkyd resin, medicine, dye, and preservatives, are usually obtained by the selective oxidation of alcohols with chlorine, organic peroxides, potassium permanganate and potassium dichromate, etc. as the oxidant [1], and a

large amount of waste will be produced unavoidably. If oxygen or air can be used as the sole oxidant, the manufacture of carboxylic acids will become green and sustainable. Noble metal catalysts have been widely investigated in the aerobic oxidation of alcohols with oxygen as the oxidant [2-9]. Among various noble metal catalysts, the Au catalysts exhibit the most promising potentials because they can smoothly catalyze this reaction under much milder conditions.

Recently, much attention has been paid to heterogeneous Au catalysts for liquid-phase fine chemical synthesis [10-17], which are typically prepared by the deposition of Au NPs onto the suitable supports via deposition-precipitation, co-precipitation, impregnation, solid grinding and other methods. In this case, the catalytic performance of the Au catalysts and the selectivity of the resulting products strongly depend on the nature of the supports, the sizes and valence of Au NPs, and the interaction between Au NPs and the supports. Specifically, the nature of the supports displays a very important role. For instance, nickel oxide supported Au catalysts were highly active for the aerobic oxidation of octanol to octanoic acid [18]. Hydrotalcite was demonstrated to be a suitable support for the oxidant- and acceptor-free dehydrogenation of benzyl alcohol to benzaldehyde than TiO₂, ZrO₂, La₂O₃ and other supports, because of its acidity and basicity [19]. In addition, SrTiO₃ supported Au catalysts were reported to exhibit an extremely high catalytic activity for the aerobic oxidation of benzyl alcohol to benzoic acid [20].

It is generally considered that small Au NPs will exhibit better catalytic performance because the ratio of the exposed surface Au atoms to total Au atoms is larger in small Au NPs [21-25]. For instance, the catalytic activity of Au catalyst increased with the decreasing size in the aerobic oxidation of glucose to gluconic acid [21,22]. Furthermore, small Au NPs possess much more coordinatively unsaturated surface Au atoms, which makes them more active for the activation of oxygen and then aerobic oxidation of substrates [26]. In addition, it was also reported that in some reactions the Au catalysts displayed an optimal size or number of Au atoms, and smaller and larger Au particles caused the reduction of catalytic activity [27,28]. However, to the best of our knowledge, the examples of the opposite phenomenon, i.e. the activity increases with the increasing size of Au particles, are still quite rare [29].

So far, the most studied support materials for the Au catalysts are inorganic oxides and carbon materials, which could only be modified within a small range. In contrast, polymers can be

functionalized as expected, thus the performance of the polymer supported catalysts could be adjusted via designing the structure, acidity/basicity and hydrophilic/hydrophobic properties of polymers. The use of polymer network to construct heterogeneous catalysts presents a promising alternative, preventing agglomeration while providing the inherent advantages of heterogeneous catalysts, such as the ease separation of the catalysts from the products and the recycling of the catalysts [29-32]. For example, Kobayashi *et al* [29]. developed the direct aerobic oxidative amide synthesis using aldehydes and amines as substrates by employing a crosslinked copolymer-incarcerated Au NPs (with different sizes) composite as the catalysts. These catalysts exhibited high activity and Au NPs with medium size gave the best performance in amide formation, meanwhile, the catalyst could be recovered without the loss of activity. Xiao *et al* [33]. used the amino-modified polydivinylbenzene as the support to immobilize Au particles (20–150 nm) and the resulting catalysts performed well in the aerobic oxidation of styrene. Therefore, the incorporation of Au NPs into open porous networks of polymers represents an attractive strategy for catalyst design.

In this work, a nitrogen-containing crosslinked polymer (poly(divinylbenzene-*co-N*-vinylimidazole, PDVB-VI-*n*) was utilized as the building blocks to anchor Au NPs by *in situ* reduction of Au ions. The catalytic activity of the resulting Au/PDVB-VI-*n* catalysts was evaluated by the aerobic oxidation of benzyl alcohol in aqueous solution under mild basic conditions using oxygen as the sole oxidant. The results indicated that the hydrophilicity/hydrophobicity of polymer and the sizes of Au NPs displayed very important roles to determine the catalytic activities and the selectivity of benzoic acid.

2. Experimental Detail

2.1 Materials

N-vinylimidazole (VI) was purchased from Aldrich and distilled under reduced pressure before use. Divinylbenzene (DVB) was purchased from Alfa Aesar and washed with the same volume of NaOH aqueous solution (0.5 M) and deionized water three times before use, respectively. Benzyl alcohol was got from Alfa Aesar. 2,2'-azobis(2-methylpropionitrile) (AIBN) and gold trichloride (AuCl₃) were obtained from Adamas-Beta Reagent Co., Ltd.

Sodium borohydride (NaBH₄), potassium carbonate (K₂CO₃), hydrochloric acid (HCl), ethyl acetate and methanol were supplied by Sinopharm Chemical Reagent Co.

2.2 Synthesis of poly(divinylbenzene-co-N-vinylimidazole)-n (PDVB-VI-n)

PDVB-VI-*n* was synthesized via a refined procedure described in the references [33,37,38] by radical crosslinking copolymerization of DVB and VI in ethyl acetate, initiated by AIBN. A typical procedure is described as follows. DVB (2.0 g, 2.18 mL), VI (0.723 g, 0.696 mL), and AIBN (0.07 g) were added into ethyl acetate (30 mL). The mixture was then placed into a flask under nitrogen atmosphere and kept at 100 °C for 24 h under static conditions. After the copolymerization, the solvent was evaporated under vacuum at 25 °C for 24 h, and then the white powder was obtained and denoted as PDVB-VI-0.33 (the molar ratio of VI to DVB is 0.33). The composition of PDVB-VI-*n* could be easily adjusted by varying the molar ratios of two monomers (*n* is the molar ratio of VI to DVB).

2.3 The preparation of PDVB-VI-n immobilized Au NPs

A typical procedure for the preparation of PDVB-VI-*n* immobilized Au NPs is described as follows. 10 mg of AuCl₃ was dissolved in 10 mL of methanol, and then 100 mg of PDVB-VI-0.33 was added to this solution under stirring. The resulting suspension was further vigorously stirred for 24 h in order that Au(III) ions could be adsorbed as much as possible.

After filtration, PDVB-VI-*n* adsorbing Au(III) ions was further transferred to 10 mL of NaBH₄ methanol solution (1 mg/mL), and stirred for 6 h to ensure the complete reduction of Au(III) ions. Finally, PDVB-VI-*n* supported Au catalysts were filtrated, washed with methanol repeatedly, and dried under vacuum for 24 h at room temperature. The obtained Au catalysts were named as *x*Au/PDVB-VI-*n*, where *x* represents Au loadings.

2.4 Aerobic oxidation of benzyl alcohol catalyzed by xAu/PDVB-VI-n

Aerobic oxidation of benzyl alcohol catalyzed by xAu/PDVA-VI-n was performed in a 10 mL flask under atmospheric pressure. In a typical reaction, benzyl alcohol (12.9 µL, 0.125 mmol), K₂CO₃ (5.19 mg, 0.0375 mmol), water (2.5 mL) and the requisite amount of xAu/PDVB-VI-n were added into the flask, and then pure O₂ was purged into the flask. The mixture was kept at

90 °C for 16 h at the stirring speed of 600 rpm. After the reaction, HCl was added into the mixture to adjust the pH to the range of 3~4, and then the mixture was extracted with ethyl acetate (1.5 mL) and centrifuged to remove the catalyst. The organic phase was analyzed by GC-MS, and the products were identified by comparison with known authentic standards. The GC yields of all the products were obtained from the calibration curves.

2.5 Characterizations

Fourier transform infrared (FTIR) spectroscopy analysis was carried out on a VERTEX 70 spectrometer (Bruker). The spectra were collected in the frequency range of 600–4000 cm⁻¹ with a resolution of 4 cm⁻¹ by averaging 32 scans. Gold loadings in xAu/PDVB-VI-n catalysts were determined by using inductively coupled plasma optical emission spectrometry (ICP-OES) (7300 DV, Perkin Elmer). Gold NPs in the fresh and used xAu/PDVB-VI-n catalysts were observed by transmission electron microscope (TEM) (JEM-2100, JEOL). Nitrogen isotherms at the temperature of liquid nitrogen were measured using a ASAP 2020 system (Micromeritics, USA). The samples were outgassed for 12 h at 80 °C before the measurement. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Temperature programmed desorption of CO₂ (CO₂-TPD) and NH₃ (NH₃-TPD) analyses of PDVB-VI-n supports were conducted on a Micromeritics AutoChem 2920II Chemisorption Analyzer. X-ray photoelectron spectroscopies (XPS) were performed on a Thermo ESCALAB 250Xi photoelectron spectrometer. The conversion of benzyl alcohol and the yields of products were determined by gas chromatography-mass spectrometer equipped with a HP-5ms column (GC-MS, 7890B GC System-5977MSD, Agilent Technologies). The products were identified by comparison with known authentic standards, and an external standard method was used for the qualitative analysis.

3. Results and Discussion

3.1 Synthesis of PDVB-VI-n and Au/PDVB-VI-n catalyst

A series of PDVB-VI-*n* with different compositions were synthesized in good yields under N_2 atmosphere through the radical crosslinking reaction of DVB and VI (with different ratios) at 100 °C without stirring for 24 h (Scheme 1). The introduction of imidazole group into the

crosslinked structure was demonstrated by FT-IR spectra. As shown in Figure 1, the absorption peak at 2927 cm⁻¹ belonged to the stretching vibration of aliphatic C–H bond. The imidazole ring possessed characteristic peaks at 1651 cm⁻¹ and 1228 cm⁻¹ due to the vibration of -C=N- and -C-N-, respectively. The peaks at 1495 cm⁻¹ and 1456 cm⁻¹ were assigned to the stretching vibration of benzene skeleton, the peaks at 904 cm⁻¹, 800 cm⁻¹ and 711 cm⁻¹ were attributed to the deformation vibration of C–H bond in benzene ring. It was clear that the intensity of peaks ascribed to imidazole ring became stronger along with the increasing of *n* value.

Gold NPs were then immobilized on the crosslinked PDVB-VI-*n* by *in situ* reduction of AuCl₃ with NaBH₄ at room temperature (Scheme 2). The positively charged Au(III) cations were firstly adsorbed on PDVB-VI-*n* via the coordination of Au(III) cations with the electron rich N atoms. The adsorbed Au(III) cations were then reduced by NaBH₄ to form Au NPs and the N atoms in the polymer could still help to anchor the Au NPs. The Au loadings of Au/PDVB-VI-*n* are listed in Table 1. It was clear that with the increase of AuCl₃ weight ratio in AuCl₃/PDVB-VI-*n*, the actual Au loadings increased quickly. The only exception was that entry 6 displayed only slight increase of Au loadings compared to entry 5. This may indicate that the coordination sites (N atoms) in entry 5 have been almost saturated by Au(III) cations, thus further increase of AuCl₃/PDVB-VI-0.33 weight ratio could cause little increase of Au loadings.

TEM images and the size distribution of Au NPs supported on four PDVB-VI-*n* (n = 0.1, 0.33, 0.67 and 1.0) were shown in Figure S1-4. These figures showed that Au NPs were highly dispersed on all the polymer supports without aggregation. As shown in Table 1 and Figure S1-4, when PDVB-VI-0.33 and PDVB-VI-0.67 were used as the supports, the mean sizes of Au NPs could be easily adjusted in the range of 2.4–4.3 nm by simply changing AuCl₃ weight ratio of AuCl₃/PDVB-VI-*n*. However, for PDVB-VI-0.1 and PDVB-VI-1.0, only relative large Au NPs were obtained, giving the mean Au sizes of 3.6 nm and larger. In addition, it was also found that on Au/PDVB-VI-0.33, Au/PDVB-VI-0.67 and Au/PDVB-VI-1.0, the mean sizes of Au NPs increased with the increase of AuCl₃ weight ratio in AuCl₃/PDVB-VI-*n*. However, the mean sizes of Au NPs VI-0.1 decreased with the increase of AuCl₃ weight ratio in AuCl₃/PDVB-VI-0.1.

The N₂ adsorption-desporption isotherms of PDVB-VI-0.1, PDVB-VI-0.33, PDVB-VI-0.67 and PDVB-VI-1.0 were shown in Figure S5. Among these four supports, PDVB-VI-0.1 had the highest N₂ uptake and the largest Brunner-Emmett-Teller (BET) sufrace area of 2016.9 m²/g (Table S1). With the increasing of *N*-vinylimidazole component, N₂ uptake and BET surface area of PDVB-VI-*n* decreased gradually. Table S1 also showed that compared with PDVB-VI-*n* supports, Au/PDVB-VI-*n* possessed lower BET surface area and smaller pore volume. This confirmed that Au NPs have been successfully introduced into the three-dimensional porous system of PDVB-VI-*n*. Figure S6 showed that the introduction of Au NPs into the three-dimensional porous system of PDVB-VI-*n* did not influence the pore size distribution, and both PDVB-VI-*n* and Au/ PDVB-VI-*n* possessed small amount of large mesopores (10-50 nm) and large amount of macropores (> 50 nm). Since Au/PDVB-VI-*n* had both three-dimensional porous system and large pores (large mesopores and macropores), the reactants and the products could efficiently diffuse into and out of the porous system. Therefore, in the following the influence of Au NPs location (on the surface or inside the porous system of Au/PDVB-VI-*n*) on the catalytic activity of Au/PDVB-VI-*n* will not be considered.

The acidity and basicity of PDVB-VI-*n* supports were determined by NH₃-TPD and CO₂-TPD in the temperature range of 45-210 °C because PDVB-VI-*n* began to decompose at 210 °C (Figure S7). No desorption peak could be observed in NH₃-TPD profiles of all the PDVB-VI-*n* supports, indicating that all the polymer supports contains no acidic sites. However, for CO₂-TPD profiles, the clear desorption peaks at about 175 °C could be found over PVDB-VI-*n* (n = 0.1, 0.33, 0.67, 1.0) except PDVB. This suggests that PVDB-VI-*n* (n = 0.1, 0.33, 0.67, 1.0) possess basic sites, which should be caused by basic imidazole groups. In addition, the area of CO₂ desorption peak tended to increase with the increasing of N-vinylimidazole ratio as expected. These basic imidazole groups introduced into PDVB-VI-*n* supports could provide N atoms to coordinate with Au(III) and then anchor Au NPs. Meanwhile, these basic imidazole groups could efficiently reduce the usage of basic reagents such as K₂CO₃ in the aerobic oxidation of benzyl alcohol over Au/PDVB-VI-*n* in comparison to normal Au catalysts. X-ray photoelectron spectroscopy (XPS) of 1.4Au/PDVB-VI-0.1, 7.7Au/PDVB-VI-0.3, 13.3Au/ PDVB-VI-0.67 and

2.6Au/ PDVB-VI-1.0 displayed two peaks at 87.67 and 84.0 eV, corresponding to Au $4f_{5/2}$ and Au $4f_{7/2}$ [34], respectively (Figure S8). These peaks indicated that Au species existed as metallic states in these four Au catalysts.

3.2 The selective catalytic oxidation of benzyl alcohol

The aerobic oxidation of benzyl alcohol was catalyzed by resultant Au/PDVB-VI-n at 90 °C for 16 hours with 1 atm oxygen as the sole oxidant and water as the solvent. GCMS results confirmed the presence of three products: benzaldehyde, benzoic acid and benzyl benzoate. The aerobic oxidation of benzyl alcohol was firstly conducted with different molar ratios of the K₂CO₃/substrate to determine the proper amount of base, and the results were summarized in Table 2. 7.7Au/PDVB-VI-0.33 possessing moderate loading amount and particle size among all 12 catalysts was chosen as the model. The oxidation of benzyl alcohol in oxygen alone failed to afford the acid without the addition of base, and the conversion of benzyl alcohol was also as low as 40.2%. The addition of base improved the yield (K₂CO₃/substrate=0.1) and benzoic acid was formed with the selectivity of 25.6%. Meanwhile, the conversion of benzyl alcohol was also greatly enhanced to 79.5%. The selectivity of benzoic acid rose up quickly with the increase of base amount, and then leveled off at around 80% at the K₂CO₃/substrate ratio of 0.3. A further increase of base amount could not promote the increase of the selectivity of benzoic acid any more. Table 2 showed that 100% conversion of benzyl alcohol was achieved at the K₂CO₃/substrate ratio of 0.3 and above. As for Au catalysts, the aerobic oxidation of alcohols to corresponding carboxylic acids usually requires the stoichiometric or even larger amount of base or strong base [35,36]. In this case, not carboxylic acids but carboxylates are produced, and thus inorganic acid such as hydrochloride acid has to be used to acidate carboxylates to carboxylic acids and neutralize the excessive amount of base, which leads to the formation of a large amount of salts as the by-products. The lower amount of base is better from the view point of actual applications,. In this work high yield of benzoic acid of 80% was otained on 7.7Au/PDVB-VI-0.33 when the molar ratio of the K₂CO₃/substrate was only 0.3, which meant that Au/PDVB-VI-n might be the promising catalysts for the aerobic oxidation of alcohols to carboxylic acids. In the following tests, the K₂CO₃/substrate ratio was fixed at 0.3.

It is well known that Au catalysis is very sensitive to the size of Au particles [21-25,27,28], for instance, in gas-phase CO oxidation [25] and in liquid-phase glucose oxidation [21,22]. In this work, we tried to investigate the influence of Au sizes on catalytic performance of Au/PVDB-VI-*n* in the aerobic oxidation of benzyl alcohol in liquid phase. Firstly, we investigated catalytic activities of 4.2 nm and 4.9 nm Au NPs supported on PDVB-VI-0.1 (Figure 2). Compared with 4.2 nm Au NPs, 4.9 nm Au NPs displayed much higher conversion of benzyl alcohol at Au/substrate ratio of 1/50, 1/100 and 1/200, respectively, indicating larger Au NPs was more beneficial to the catalytic oxidation of benzyl alcohol. However, regarding the selectivity of benzoic acid, 4.2 nm Au NPs and 4.9 nm Au NPs gave the similar but low selectivity of about 20% at Au/substrate ratio of 1/50 and 1/100. When Au/substrate ratio decreased to 1/200, benzaldehyde was the only product, and the conversion of benzyl alcohol was also very low, less than 20%.

Figure 3 showed the influence of Au sizes on the conversion of benzyl alcohol and the selectivity of products on Au/PDVB-VI-0.33. It was clear that with the increase of Au sizes, the conversion of benzyl alcohol increased monotonously. In addition, the selectivity of benzoic acid was tightly related to the size of Au NPs. A markedly volcano curve could be clearly observed by plotting the sizes of Au NPs and the selectivity of benzoic acid. The highest selectivity of benzoic acid of 80.6% was achieved on 3.2 nm Au NPs. Smaller and larger Au NPs would lead to lower selectivity of benzoic acid. Similar phenomenon was also observed over Au/PDVB-VI-0.67 (Figure 4). Figure 5 showed the influence of Au sizes on the conversion of benzyl alcohol and the selectivity of products on Au/PDVB-VI-1.0. It was clear that with the increase of Au sizes from 3.6 nm to 3.9 nm, the conversion of benzyl alcohol decreased slightly and the selectivity of benzoic acid was almost the same.

Based on the results above, it can be inferred that in the aerobic oxidation of benzyl alcohol on Au/PDVB-VI-*n*, the conversion of benzyl alcohol and the selectivity of products are tightly related to the composition of PDVB-VI-*n* and the sizes of Au NPs when the ratio of Au/substrate is fixed. By comparing the catalytic activities of Au NPs supported on different PDVB-VI-*n* polymer in Figure 2-5, it can be concluded that Au NPs supported on PDVB-VI-0.33, 0.67 and

1.0 shows much better catalytic activities than the ones supported on PDVB-VI-0.1. This could be explained as follows. PDVB-VI-n polymer supports were synthesized from hydrophobic divinylbenzene (DVB) and hydrophilic N-vinylimidazole (VI), and thus Au/PDVB-VI-n possessed both hydrophobic and hydrophilic structures. The hydrophilic groups in Au/PDVB-VI-*n* tended to stay on the outer part of the supports to have a contact with water. When n = 0.1, the amount of hydrophilic groups were quite small, the contact between supports and water was not enough, thus Au/PDVB-VI-0.1could not disperse well in water and its catalytic activity was low. However, when n = 033, 0.67 and 1.0, the hydrophilic groups were enough to generate a good contact between supports and water, thus the corresponding Au catalysts performed well. On the other hand, the hydrophobic groups in Au/PDVB-VI-n tended to be located in the inner part of the supports and form the hydrophobic domain. Benzyl alcohol possessed a similar structure to polymer skeleton and relative hydrophobic property, and thus the hydrophobic domain inside Au/PDVB-VI-n (n = 033, 0.67 and 1.0) can remarkably enhance the local concentration of benzyl alcohol according to "like dissolves like" rule and thus accelerate the catalytic oxidation of benzyl alcohol. Therefore, it is clear that the achievement of excellent catalytic performance of Au/PDVB-VI-n requires a good balance between hydrophilic N-vinylimidazole groups and hydrophobic divinylbenzene groups in polymer matrix. The intrinsic structural characteristic of the crosslinked polymer support guarantee the well dispersion of Au/PDVB-VI-n in water solvent and the enrichment of substrates inside the polymer matrix of Au/PDVB-VI-n.

It is usually observed that the conversion of substrates increases markedly with the decrease of the size of Au NPs [21-25], for example, in the oxidation of CO to CO_2 [25] and in the aerobic oxidation of glucose to gluconic acid [21,22]. This can be reasonably explained that with the decrease of the sizes of Au NPs, the ratio of the exposed surface Au atoms to total Au atoms will increase, and the number of active surface Au atoms will increase, which finally leads to the enhancement of catalytic performance of the supported Au catalysts. In addition, it is also assumed that surface Au atoms of smaller Au NPs possess lower coordination number than larger Au NPs, especially on the edge and corner positions. Thus, smaller Au NPs are much more active for the activation of oxygen and then the aerobic oxidation of substrates than larger Au

NPs [26]. However, in this work, with the decrease of the sizes of Au NPs, especially on Au/PDVB-VI-0.33 and Au/PDVB-VI-0.67, the conversion of benzyl alcohol did not increase but decreased remarkably. Until now the reason for this phenomenon is not clear yet. However, it indicates that the reaction mechanism involved in aerobic oxidation of benzyl alcohol on Au/PDVB-VI-*n* may be different from that involved in CO oxidation and glucose oxidation catalyzed by the supported Au catalysts. Therefore, further efforts will be devoted to exploring the possible reaction mechanism of aerobic oxidation of benzyl alcohol on Au/PDVB-VI-*n*.

In order to study the effect of the sizes of Au NPs on the selectivity of products, three couples of catalysts were chosen, 1.9Au/PDVB-VI-0.33 vs. 2.5Au/PDVB-VI-0.67, 7.7Au/PDVB-VI-0.33 vs. 13.3Au/PDVB-VI-0.67, and 17.4Au/PDVB-VI-0.67 vs. 8.0Au/PDVB-VI-1.0. As listed in Table 3, when the sizes of Au NPs were similar and the selectivities towards benzaldehyde, benzoic acid and benzyl benzoate were also similar, regardless of the type and amount of the polymer supports and the molar ratio of Au to substrate. This confirms that the product distributions are mainly determined by the sizes of Au NPs. When Au NPs were 2.4 nm, only a moderate selectivity of benzoic acid less than 50% was obtained. Interestingly, with the increase of the size of Au NPs from ~2.4 nm to ~3.2 nm the selectivity towards benzyl benzoate decreased markedly and the selectivity towards benzoic acid increased remarkably (entry 1 and 6). The highest selectivity of benzoic acid of around 80% was achieved over ~3.2 nm Au NPs supported on 7.7Au/PDVB-VI-0.33 and 13.3Au/PDVB-VI-0.67, together with the high conversion of benzyl alcohol, > 90%. Whereas a further increase of Au sizes to ~3.9 nm led to a dramatically decrease in the selectivity of benzoic acid (entry 1, 6 and 11).

In order to carefully investigate the evolution of the conversion of benzyl alcohol and the selectivity towards three products over the reaction time, four catalysts prepared with the same support (PDVB-VI-0.67) were chosen to catalyze the aerobic oxidation of benzyl alcohol under the same conditions at a relatively low Au/substrate ratio (1/200) to distinguish the different behavior of four catalyst more clearly (Figure 6). For all the four catalysts, the conversions grew up quickly with the reaction time at initial stage and reached over their extreme value at about 4 hours, then the conversion curves leveled off. Over all the four catalysts, benzaldehyde and

benzyl benzoate were always produced as the main products at the initial reaction stage, and then their selectivities decreased rapidly with the reaction time. However, benzoic acid exhibited different evolution tendencies regarding its selectivity over the four Au catalysts. Over 13.3Au/PDVB-VI-0.67 and 17.4Au/PDVB-VI-0.67, benzoic acid was produced once the reaction began, and its selectivity increased gradually with the reaction time. However, over 2.5Au/PDVB-VI-0.67 and 6.2Au/PDVB-VI-0.67, benzoic acid was not produced in the initial 4 hours. With the extension of reaction time benzoic acid began to be produced and its selectivity increased rapidly with the reaction time.

Finally, a possible reaction pathway was proposed for the aerobic oxidation of benzyl alcohol over Au/PDVB-VI-0.67 (Scheme 3). It was assumed that four important steps needed to be considered: 1) the aerobic oxidation of benzyl alcohol to benzaldhyde; 2) the aerobic oxidation of benzyl alcohol to benzaldehyde to benzoic acid; 3) the oxidative esterification of benzaldehyde with benzyl alcohol to benzyl benzoate; 4) the hydrolysis of benzyl benzoate to benzoic acid and benzyl alcohol in the presence of base (K₂CO₃ and *N*-vinylimidazole). Among these four steps, step [2] and step [4] would lead to the formation of benzoic acid. As for 2.5Au/PDVB-VI-0.67 and 6.2Au/PDVB-VI-0.67, benzoic acid might be produced through step [4], where benzoic acid was formed by the hydrolysis of benzyl benzoate. If benzoic acid was produced by the oxidation of benzaldhyde was produced once the aerobic oxidation of benzyl alcohol was initiated (Figure 6). However, as for 13.3Au/PDVB-VI-0.67 and 17.4Au/PDVB-VI-0.67, benzoic acid was produced by the oxidation of benzyl alcohol was produced through step [2] and [4], where benzoic acid was produced by the oxidation of benzyl alcohol was produced through step [2] and [4], where benzoic acid was produced by the oxidation of benzyl alcohol was produced through step [2] and [4], where benzoic acid was produced by the oxidation of benzyl alcohol was produced by the oxidation of benzyl alcohol was produced through step [2] and [4], where benzoic acid was produced by the oxidation of benzyl benzoate.

4. Conclusions

Different amounts of imidazole groups were introduced into the crosslinked polymer network via copolymerization and the copolymer was employed as the supports to immobilize Au NPs. TEM characterizations confirmed that Au NPs were highly dispersed on the polymer matrix and

their sizes could be easily adjusted by changing the weight ratio of AuCl₃ in AuCl₃/PDVB-VI-*n*. The prepared Au/PDVB-VI-*n* catalysts were then applied in the aerobic oxidation of benzyl alcohol under oxygen in alkaline aqueous solution. The results indicated that the size of Au NPs remarkably influenced the conversion of benzyl alcohol and the selectivity of products. The conversion of benzyl alcohol increased along with the increase of Au NP sizes within the range of 2–5 nm, while the selectivity of benzoic acid displayed a volcano curve versus the sizes of Au NPs. ~3.2 nm Au NPs supported on PDVB-VI-0.33 and PDVB-VI-0.67 gave the highest selectivity of benzoic acid of around 80% together with the high conversions of benzyl alcohol of >90% when only a small amount of base was introduced (K₂CO₃/substrate = 0.3). A possible reaction pathway was proposed for the aerobic oxidation of benzyl alcohol on Au/PDVB-VI-0.67, which indicated that benzoic acid could be produced by the hydrolysis of benzyl benzoate under basic conditions as well as by the selective oxidation of benzaldehydes.

Supporting Information

Additional characterization information including TEM images and size distributions of Au/PDVB-VI-*n* catalysts are presented in detail.

Notes

The authors declare no competing financial interest.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (No.21606220 and No. 21473186), the Young Thousand Talents Program of China, and the "Strategic Priority Research Program" of the Chinese Academy of Sciences (XDA09030103).

References

- G. Cainelli, G. Cardillo, Chromium Oxidant in Organic Chemistry, Springer Verlag, Berlin, 1984.
- [2] N. Dimitratos, J. A. Lopez-Sanchez, G. J. Hutchings, Chem. Sci. 3 (2012), 20-44.
- [3] A. Biffis, L. Minati, J. Catal. 236 (2005), 405-409.
- [4] A. Abad, C. Almela, A. Corma, H. Garcia, Tetrahedron, 62 (2006), 6666-6672.
- [5] L. Han, P. Xing, B. Jiang, Org. Lett. 16 (2014), 3428-3431.
- [6] B. N. Zope, D. D. Hibitts, M. Neurock, R. J. Davis, Science, 330 (2010), 74-78.
- [7] F. Kerdi, H. A. Rass, C. Pinel, M. Besson, G. Peru, B. Leger, S. Rio, E. Monflier, A. Ponchel, Appl. Catal. A, 506 (2015), 206-219.
- [8] Y. M. A. Yamada, T. Arakawa, H. Hocke, Y. Uozumi, Angew. Chem. Int. Ed. 46 (2007), 7 04-706.
- [9] S. E. Davis, M. S. Ide, R. J. Davis, Green Chem. 15 (2013), 17-45.
- [10] A. Corma, H. Garcia, Chem. Soc. Rev. 37 (2008), 2096-2126.
- [11] C. Della Pina, E. Falletta, L. Prati, M. Rossi, Chem. Soc. Rev. 37 (2008), 2077-2095.
- [12] A. Abad, P. Concepcion, A. Corma, H. Garcia, Angew. Chem.Int. Ed. 44 (2005), 4066-4069.
- [13] L. Liu, Y. Song, H. Chong, S. Yang, J. Xiang, S. Jin, X. Kang, J. Zhang, H. Yu, M. Zhu, Nanoscale, 8 (2016), 1407-1412.
- [14] J. Ftouni, M. Penhoat, J. Girardon, A. Addad, E. Payen, C. Rolando, Chem. Eng. J. 227 (2013), 103-110.
- [15] Y. He, J. Feng, G. L. Brett, Y. Liu, P. J. Miedzia, J. K. Edwards, D. W. Knight, D. Li, G. J. Hutchings, ChemSusChem, 8 (2015), 3314-3322.
- [16] C. J. Davies, P. J. Miedziak, G. L. Brett, G. J. Hutchings, Chinese J. Catal. 37 (2016),

1600-1607.

- [17] H. Miyamura, S. Isshiki, H. Min, S. Kobayashi. Chinese J. Catal. 37 (2016), 1662-1668.
- [18] T. Ishida, Y. Ogihara, H. Ohashi, T. Akita, T. Honma, H. Oji, M. Haruta, ChemSusChem, 5 (2012), 2243-2248.
- [19] W. H. Fang, J. S. Chen, Q. H. Zhang, W. P. Deng, Y. Wang, Chem. Eur. J. 17 (2011), 1247-1256.
- [20] S. Naya, M. Teranishi, R. Aoki, H. Tada, J. Phys. Chem. C, 120 (2016), 12440-12445.
- [21] T. Ishida, N. Kinoshita, H. Okatsu, T. Akita, T. Takei, M. Haruta, Angew. Chem. Int. Ed. 47 (2008), 9265-9268.
- [22] M. Comotti, C. Della Pina, R. Matarrese, M. Rossi, Angew.Chem. Int. Ed. 43 (2004), 5812-5815.
- [23] A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, Angew. Chem. Int. Ed. 50 (2011), 2986-2989.
- [24] H. Tsunoyama, N. Ichikuni, H. Sakurai, T. Tsukuda, J. Am. Chem. Soc. 131 (2009), 7086-7093.
- [25] T. Fujitani, I. Nakamura, Angew. Chem. Int. Ed. 50 (2011), 10144-10147.
- [26] M. Turner, V. B. Golovko, O. P. H. Vaughan, P. Abdulkin, A. Berenguer-Murcia, M. S. Tikhov, B. F. G. Johnson, R. M. Lambert, Nature, 454 (2008), 981-984.
- [27] Y. M. Liu, H. Tsunoyama, T. Akita, S. H. Xie, T. Tsukuda, ACS Catal. 1 (2011), 2-6.
- [28] N. F. Zheng, G. D. Stucky, J. Am. Chem. Soc. 128 (2006), 14278-14280.
- [29] H. Miyamura, H. Min, J. Soule. S. Kobayashi, Angew. Chem. Int. Ed. 54 (2015), 7564-7567.
- [30] H. Yuan, W. Yoo, H. Miyamura, S. Kobayashi, J. Am. Chem. Soc. 134 (2012), 13970-13973.
- [31] W. Yoo, H. Miyamura, S. Kobayashi, J. Am. Chem. Soc. 133 (2011), 3095-3103.

- [32] Y. Lu, S. Proch, M. Schrinner, M. Drechsler, R. Kempe, M. Ballauff, J. Mater. Chem. 19 (2009), 3955-3961.
- [33] L. Wang, B. Zhang, W. Zhang, J. Zhang, X. Gao, X. Meng, D. Su, F. Xiao, Chem. Commun. 49 (2013), 3449-3451.
- [34] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, Handbook of X-ray photoelectron spectroscopy, Perkin-Elmer Corporation, physical electronics division, Minnesota, 1979.
- [35] C. P. Ferraz, M. A. S. Garcia, E. T. Teixeira-Neto, L. M. Rossi, RSC Adv. 6 (2016), 25279-25285.
- [36] S. Rautiainen, O. Simakova, H. Guo, A. Leino, K. Kodas, D. Murzin, M. Leskela, T. Repo, App. Catal. A, 485 (2014), 202-206.
- [37] F. Liu, W. Li, Q. Sun, L. Zhu, X. Meng, Y. Guo, F. Xiao, ChemSusChem, 4 (2011), 1059-1062.
- [38] Y. Zhang, S. Liu, F. Liu, H. Zhang, Y. He, F. Xiao, Catal. Commun. 12 (2011), 1212-1217.



Figure 1. FT-IR spectra of PDVB-VI-n with different compositions



Figure 2. Influence of the size of Au NPs on catalytic activities of Au/PDVB-VI-0.1 in the aerobic oxidation of benzyl alcohol at the Au/substrate ratio of 1/50, 1/100 and 1/200, respectively. Aldehyde: benzaldehyde; acid: benzoic acid; ester: benzyl benzoate. The percentages represent the Au loadings and the mean Au sizes are given beneath the Au loadings.



Figure 3 Influence of the size of Au NPs on catalytic activities of Au/PDVB-VI-0.33 in the aerobic oxidation of benzyl alcohol at the Au/substrate ratio of 1/100. Aldehyde: benzaldehyde; acid: benzoic acid; ester: benzyl benzoate. The percentages represent the Au loadings and the mean Au sizes are given beneath the Au loadings.



Figure 4. Influence of the size of Au NPs on catalytic activities of Au/PDVB-VI-0.67 in the aerobic oxidation of benzyl alcohol at the Au/substrate ratio of 1/100. Aldehyde: benzaldehyde; acid: benzoic acid; ester: benzyl benzoate. The percentages represent the Au loadings and the mean Au sizes are given beneath the Au loadings.



Figure 5. Influence of the size of Au NPs on catalytic activities of Au/PDVB-VI-1.0 in the aerobic oxidation of benzyl alcohol at the Au/substrate ratio of 1/100. Aldehyde: benzaldehyde; acid: benzoic acid; ester: benzyl benzoate. The percentages represent the Au loadings and the mean Au sizes are given beneath the Au loadings.



Figure 6. Aerobic oxidation of benzyl alcohol with the reaction time on different Au catalysts prepared with the same support PDVB-VI-0.67. Benzyl alcohol conversion A) and selectivity towards benzaldehyde B) benzylic acid C) and benzyl benzoate D) in terms of the reaction time. The reactions were carried out at the Au/substrate ratio of 1/200. Aldehyde: benzaldehyde; acid: benzoic acid; ester: benzyl benzoate.



Scheme 1. The preparation of PDVB-VI-*n*



Scheme 2. The immobilization of Au NPs on PDVB-VI-*n*



Scheme 3. The possible reaction pathway for the aerobic oxidation of benzyl alcohol on Au/PDVB-VI-0.67 in water.

Entry	AuCl ₃ (mg /100 mg PDVB-VI- <i>n</i>)	Au Loadings (%) ^[a]	Catalysts	Mean Au sizes (nm)
1	5	1.4	1.4Au/PDVB-VI-0.1	4.9 ± 0.9
2	10	2.8	2.8Au/PDVB-VI-0.1	4.2 ± 1.0
3	5	1.9	1.9Au/PDVB-VI-0.33	2.4 ± 0.7
4	20	7.7	7.7Au/PDVB-VI-0.33	3.2 ± 0.8
5	30	11.1	11.1Au/PDVB-VI-0.33	3.9 ± 1.0
6	40	11.6	11.6Au/PDVB-VI-0.33	4.3 ± 1.2
7	5	2.5	2.5Au/PDVB-VI-0.67	2.5 ± 0.9
8	10	6.2	6.2Au/PDVB-VI-0.67	2.9 ± 0.9
9	30	13.3	13.3Au/PDVB-VI-0.67	3.3 ± 1.1
10	40	17.4	17.4Au/PDVB-VI-0.67	3.9 ± 1.1
11	5	2.6	2.6Au/PDVB-VI-1.0	3.6 ± 1.0
12	10	8.0	8.0Au/PDVB-VI-1.0	3.9 ± 1.0

 Table 1.
 Au loadings of Au/PDVB-VI-n catalysts

[a] The actual Au loadings of Au/PDVB-VI-*n* determined by ICP analysis.

 Table 2. Effect of K₂CO₃/substrate molar ratio on the aerobic oxidation of benzyl alcohol on

 7.7Au/PDVB-VI-0.33 in water^[a]

KaCOa/substrate		Selectivity (%)			
(mol/mol)	Conv (%)	Benzyl	Benzoic	Benzyl	
		aldehyde	acid	benzoate	
0.0	40.2	52.1	—	47.9	
0.1	79.5	30.6	25.6	43.8	
0.2	96.7	15.4	41.5	43.1	
0.3	100.0	5.6	80.5	13.9	
0.5	100.0	0.5	79.0	20.5	
1.0	100.0	1.2	83.0	15.8	

[a] The molar ratio of Au/substrate is 1/50.

Entry	Catalyst	Au/ Substrate (mol/mol)	Conv (%)	Selectivity(%)		
				aldehyde	acid	ester
1	1.9Au/PDVB-VI-0.33 ^[a]	1/50	97.3	10.5	49.4	40.1
2	2.5 Au/PDVB-VI-0.67 ^[a]	1/50	96.9	9.2	49.0	41.8
3	1.9Au/PDVB-VI-0.33 ^[a]	1/100	80.2	17.2	37.9	44.9
4	2.5 Au/PDVB-VI-0.67 ^[a]	1/100	71.2	21.1	42.5	36.4
5	7.7 Au/PDVB-VI-0.33 ^[b]	1/50	100.0	5.6	80.6	13.9
6	13.3 Au/PDVB-VI-0.67 ^[b]	1/50	99.5	4.3	81.4	14.3
7	7.7 Au/PDVB-VI-0.33 ^[b]	1/100	90.6	14.8	71.9	13.4
8	13.3 Au/PDVB-VI-0.67 ^[b]	1/100	93.6	13.2	79.5	7.3
9	7.7 Au/PDVB-VI-0.33 ^[b]	1/200	91.6	13.2	80.1	6.7
10	13.3 Au/PDVB-VI-0.67 ^[b]	1/200	92.2	9.7	76.9	13.4
11	17.4 Au/PDVB-VI-0.67 ^[c]	1/50	98.8	9.3	58.1	32.6
12	8.0 Au/PDVB-VI-1 ^[c]	1/50	93.5	8.3	60.9	30.8
13	17.4 Au/PDVB-VI-0.67 ^[c]	1/100	99.4	7.0	68.6	24.4
14	8.0 Au/PDVB-VI-1 ^[c]	1/100	91.0	14.0	55.9	30.1

Table 3. The relation of substrate conversion and product selectivity with the sizes of Au NPs inthe aerobic oxidation of benzyl alcohol on Au/PDVB-VI-n.

Aldehyde: benzaldehyde; acid: benzoic acid; ester: benzyl benzoate.

[a] The mean diameter of the Au NPs in catalysts is ~2.4 nm.

[b] The mean diameter of the Au NPs in catalysts is ~3.2 nm.

[c] The mean diameter of the Au NPs in catalysts is ~3.9 nm.