

Deposition of Gold Clusters on Porous Coordination Polymers by Solid Grinding and Their Catalytic Activity in Aerobic Oxidation of Alcohols

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Gold has turned out to be one of the most attractive elements in catalysis research since the discovery of CO oxidation at -70°C over Au nanoparticles (NPs) supported on base metal oxides.^[1] During the last decade, Au NPs supported on metal oxides^[2] and activated carbons (AC)^[3] have been widely studied for liquid phase reactions.^[4] In liquid phase reactions, catalytic performance of Au particles is mainly defined by two major factors: i) the nature of supports and ii) the size of Au particles. In particular, the size of 2 nm appears to be a critical point, where the Au particles dramatically change their catalytic and physicochemical properties.^[5] However, the conventional deposition–precipitation method is not applicable to AC due to the acidic nature of AC. Mixing Au colloids with AC could hardly give Au clusters with a diameter smaller than 2 nm. A latest trend in the selection of supports is the use of organic polymers.^[6–8] Recently, some organic polymers were found to be effective to stabilize colloidal Au in a cluster size, which showed high catalytic activity for aerobic oxidation of alcohols at room temperature.^[7] However, a constraint is that sophisticated synthetic techniques are usually required to obtain Au clusters.

On the other hand, porous coordination polymers (PCPs) consisting of metal ions and organic ligands with highly regular nanometer-sized cavities or channels are an emerging class of porous materials.^[9] They are expected to be efficient supports for metal clusters to control size and shape by means of their cavities.^[10–12] In addition, PCPs have a wide variety of porous structures, various kinds of components, and surface properties which would lead to tailor-made catalysts for the desired reactions. Thus, investigations of the preparation methods for PCP supported Au clusters and the support effect of PCPs would offer a new frontier in catalysis by Au. Fischer and co-workers have reported the preparation of Pd, Cu, Ru clusters, and Au NPs stabilized by Zn-containing PCP, MOF-5 ($[\text{Zn}_4\text{O}(\text{bdc})_3]_n$ (bdc = benzene-1,4-dicarboxylate)^[13] by chemical vapour deposition (CVD).^[11] Although Au particles could be hardly deposited in cluster size, they were obtained as NPs in the range of 5 to 20 nm on MOF-5 due to weak interaction.^[11,12] Therefore, the generation of Au clusters that fit in and/or on the cavities of PCPs is still a challenging research target.

Herein we report a very simple but the most effective method for the direct deposition of Au clusters onto several kinds of PCPs including MOF-5 by solid grinding with a volatile organogold complex without using organic solvents. We also investigated their catalytic properties for the liquid phase alcohol oxidation with molecular oxygen. To the best of our knowledge, catalysis of PCP supported Au clusters in liquid phase has not yet been studied.

The PCP supports used were one-dimensionally channelled PCPs such as CPL-1 ($[\text{Cu}_2(\text{pzdc})_2(\text{pyz})]_n$, pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine),^[14] CPL-2 ($[\text{Cu}_2(\text{pzdc})_2(\text{bpy})]_n$, bpy = 4,4'-bipyridine),^[14] AI-MIL53 ($[\text{Al}(\text{OH})(\text{bdc})]_n$)^[15] with pores of 4×6 , 6×8 , $8.5 \times 8.5 \text{ \AA}^2$, respectively, and three-dimensional PCPs such as MOF-5 and Cu-BTC ($[\text{Cu}_3(\text{btc})_2]_n$ (btc = benzene-1,3,5-tricarboxylate)^[16] with pores of 15×15 and $11 \times 11 \text{ \AA}^2$, respectively. Volatile organogold complex, $\text{Me}_2\text{Au}(\text{acac})$ (acac = acetylacetonate) and PCPs were ground in an agate mortar in air for 20 min at room temperature. Then the mixture was treated in a stream of 10 vol% H_2 in N_2 at 120°C for 2 h to obtain Au/

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PCPs by solid grinding (SG)).^[17] For comparison, supported Au catalysts were also prepared by CVD^[18] and by the deposition reduction from an aqueous solution containing HAuCl_4 and NaBH_4 .^[19]

As typically shown by Au/CPL-2 in Figure 1a, SG gave small Au particles in a nearly uniform cluster size with a mean diameter of 2.2 nm and a standard deviation of 0.3 nm (Figure 1b). On the contrary, CVD yielded larger Au NPs in addition to Au clusters. The average diameter was 3.1 nm with much wider standard deviation of 1.9 nm (Figure 1c, d). In the SG method, the sublimation of $\text{Me}_2\text{Au}(\text{acac})$ might occur during grinding and the rapid diffusion of the vapour yielded uniform distribution of the Au precursors. However, CVD took longer time (ca. 6 h) for the complete vaporization of $\text{Me}_2\text{Au}(\text{acac})$. The diffusion of $\text{Me}_2\text{Au}(\text{acac})$ vapour through the support was not uniform during CVD without agitation of powder support. This might cause the agglomeration of Au precursor and the particle growth at densely adsorbed sites to form larger NPs. Liquid-phase deposition (deposition–reduction method) caused the formation of Au colloids both on the PCP surfaces and in aqueous solution yielding only Au aggregates on PCPs.

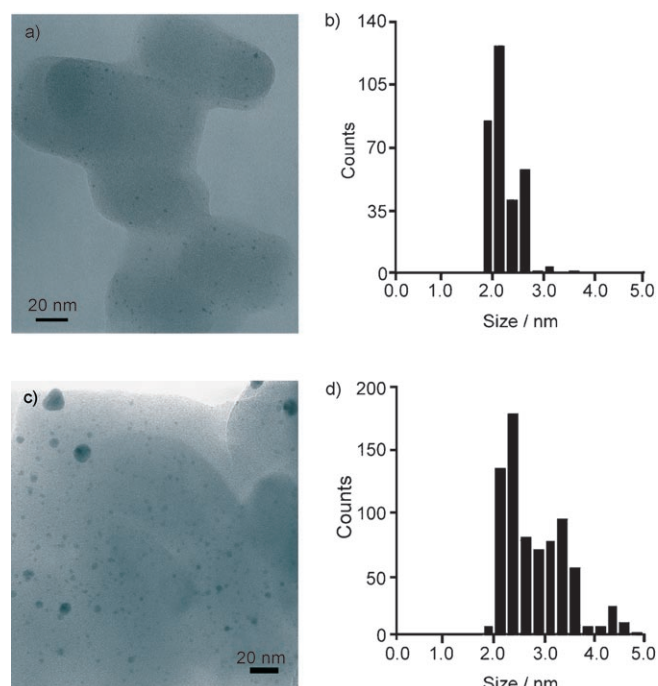


Figure 1. TEM images of Au/CPL-2 prepared by a) SG (Au 1 wt %) and c) CVD (Au 0.5 wt %) and b) the size distributions of Au/CPL-2 prepared by b) SG (Au 1 wt %), and d) by CVD (Au 0.5 wt %).

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image more clearly shows the presence of small Au clusters less than 2 nm (Figure 2a). Among the PCP supports used in this work, Al-MIL53 could support Au clusters with the smallest size of below 1 nm, resulting in a mean diameter of 1.5 nm with a standard deviation of 0.7 nm (Figure 2). Surface plasmon

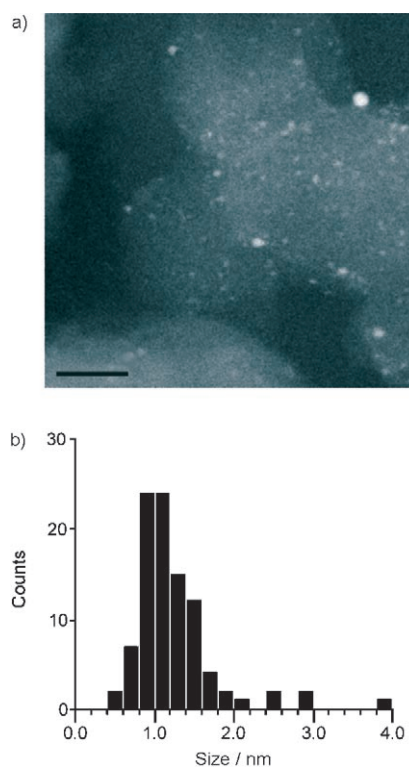


Figure 2. a) HAADF-STEM image (the scale bar indicates 10 nm) and b) size distribution of 1 wt % Au/Al-MIL53 (SG).

peaks at around 520 nm which can be ascribed to Au NPs larger than 2 nm were not observed for 1 wt % Au/Al-MIL53, showing that majority of the Au particles were in cluster size.^[19]

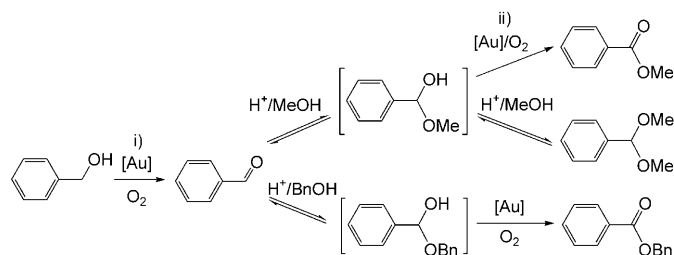
The specific surface area obtained by the N_2 adsorption isotherms of 0.5 wt % Au/CPL-2 prepared by SG and CVD were reduced to 64 and 123 m^2g^{-1} , respectively, from about 500 m^2g^{-1} of as-synthesized CPL-2.^[19] From TEM observations, Au clusters were found to be larger than the pore size and were mostly placed on the outer surfaces of PCPs. Therefore, the appreciable decrease in specific surface area observed indicates the pore blocking by Au clusters and the partial degradation of porous structure. However, the XRD (X-ray diffraction) patterns of PCPs did not change after the treatment with $\text{Me}_2\text{Au}(\text{acac})$ and the deposition of Au.^[19] This indicates that the majority of regular pore structures remained after the deposition of Au. The peak at 38° corresponding to Au(111) was not detected for 1 wt % Au/CPL-2 (SG) due to the small size of Au. Analyses by energy dispersive X-ray spectroscopy (EDX) and the absence of Cu(111) peak at 44° (2θ) in XRD proved that Cu^{II} in the framework of Cu-PCPs was not reduced to large metallic Cu^0 particles during the H_2 treatment at 120°C except for Cu-BTC.

The size of Au strongly depended on the kind of PCPs; metallic species, porous structures, and pore size.^[19] Gates and co-workers have investigated the mechanism of the ligand exchange of $\text{Me}_2\text{Au}(\text{acac})$ with the surface hydroxyl

groups of Al_2O_3 and adsorbed H_2O molecules.^[20] Okumura et al. previously reported the possibility of hydrogen bonding between oxygen atoms of $\text{Me}_2\text{Au}(\text{acac})$ and hydroxyl groups at the surface of SiO_2 .^[18] A similar ligand exchange can be assumed to occur during the diffusion of $\text{Me}_2\text{Au}(\text{acac})$ vapour in both SG and CVD between $\text{Me}_2\text{Au}(\text{acac})$ and uncoordinated carboxylate groups, metal sites at the crystal surfaces of PCPs, and surface adsorbed H_2O . Since porous frameworks fix the position of both metal-coordinating sites and carboxylate linker groups with high regularity even at the outer surfaces, metallic species, porous structures, and pore size of PCPs could mainly determine the size of Au particles and prevent them from aggregation. Generation of Au clusters at the outer surfaces of PCPs is not discouraging but beneficial in catalytic applications that involve diffusion-controlled mechanisms owing to the rapid diffusion of substrates to the Au catalytic sites.

Catalytic performance of Au/CPL-2 was first tested for the gas phase CO and H_2 oxidation.^[19] Even though the size of Au clusters is as small as 2.1 nm, Au/CPL-2 was not catalytically active in the oxidation of neither CO nor H_2 . This result was surprising but could be predicted based on the reaction mechanism of CO oxidation. We thus propose that the oxygen activation takes place at the perimeter interfaces around Au NPs with the metal oxide supports.^[5,21] Porous coordination polymers, carbons, and conventional organic polymers will not generate oxygen vacancy sites on the perimeter interfaces, resulting in poor catalytic activity in the gas phase oxidation.

In contrast to gas phase, Au/PCPs exhibited high catalytic activity for the aerobic oxidation of alcohols in the liquid phase. Table 1 shows the results of benzyl alcohol oxidation in methanol with Au/PCPs to yield benzaldehyde and methyl benzoate (Scheme 1). Two characteristic features are: i) the selection of PCP supports significantly affected catalytic activity and product selectivity, and ii) catalytic ac-



Scheme 1. Oxidation of benzyl alcohol in methanol.

tivity of Au/PCPs was superior to Au/AC and Au/ SiO_2 under base-free condition.

Firstly, Au/CPL-2 catalysts gave benzaldehyde as the main product and Au/CPL-2 (SG) (entry 10) was more active than Au/CPL-2 (CVD) (entry 9) owing to the smaller size of Au clusters. In contrast, Au/MOF-5 showed the highest catalytic activity to obtain methyl benzoate in a yield of 91% at a full conversion in the presence of K_2CO_3 within 3 h in spite of the largest size of Au particles (4.8 nm) (entry 3). The remaining 9% might be due to the adsorption of benzyl alcohol. From these results, the selection of PCP supports and the preparation method to obtain small size of Au clusters appeared to be the important factors. The turnover frequency (TOF) of Au/MOF-5 at 80 °C was calculated to be 82 h^{-1} per loaded Au atoms from the results of entry 2. Biffis et al. reported a high TOF value as high as 960 h^{-1} at 60 °C for the initial 15 min in the benzyl alcohol oxidation over Au/polymer gel in the presence of NaOH in water.^[8a] However, selectivity was low as 36% to benzoic acid and 49% to benzaldehyde, respectively.

A surprising product selectivity of benzaldehyde or methyl benzoate was observed, which dramatically changed with the PCP support. The two catalysts Au/MOF-5 and Au/Al-MIL53 were selective to methyl benzoate, which is gen-

Table 1. Oxidation of benzyl alcohol catalyzed by Au/PCPs.^[a]

Run	Catalyst	Preparation ^[b]	Base	Au [mol %]	<i>t</i> [h]	Conversion ^[c] [%]	Yield [%] ^[c]				
							PhCHO	PhCO ₂ Me	PhCO ₂ Bn	PhCO ₂ H	PhCH(OMe) ₂
1	MOF-5 ^[d]	–	K_2CO_3	0	18	0	0	0	0	0	
2	Au/MOF-5	SG	K_2CO_3	1	1	82	3	66	0	0	
3	Au/MOF-5	SG	K_2CO_3	1	3	>99	0	91	0	0	
4	Al-MIL53 ^[d]	–	K_2CO_3	0	23	0	0	0	0	0	
5	Au/Al-MIL53	SG	K_2CO_3	1	23	98	2	77	trace	0	
6	CPL-1 ^[d]	–	K_2CO_3	0	23	41	17	0	0	0	
7	Au/CPL-1	SG	K_2CO_3	1	23	45	26	0	0	0	
8	CPL-2 ^[d]	–	K_2CO_3	0	23	37	18	0	0	0	
9	Au/CPL-2	CVD	K_2CO_3	1	23	51	37	1	0	0	
10	Au/CPL-2	SG	K_2CO_3	1	23	55	43	1	0	0	
11	Cu-BTC ^[d]	–	K_2CO_3	0	23	26	6	0	0	0	
12	Au/Cu-BTC	SG	K_2CO_3	1	3	70	48	3	trace	0	
13	Au/AC	SG	K_2CO_3	1	1	>99	0	86	0	0	
14	Au/MOF-5	SG	none	1	3	69	31	23	trace	0	
15	Au/AC	SG	none	1	3	12	4	trace	trace	0	
16	Au/ SiO_2 ^[e]	SG	none	0.5	3	25	12	8	trace	0	

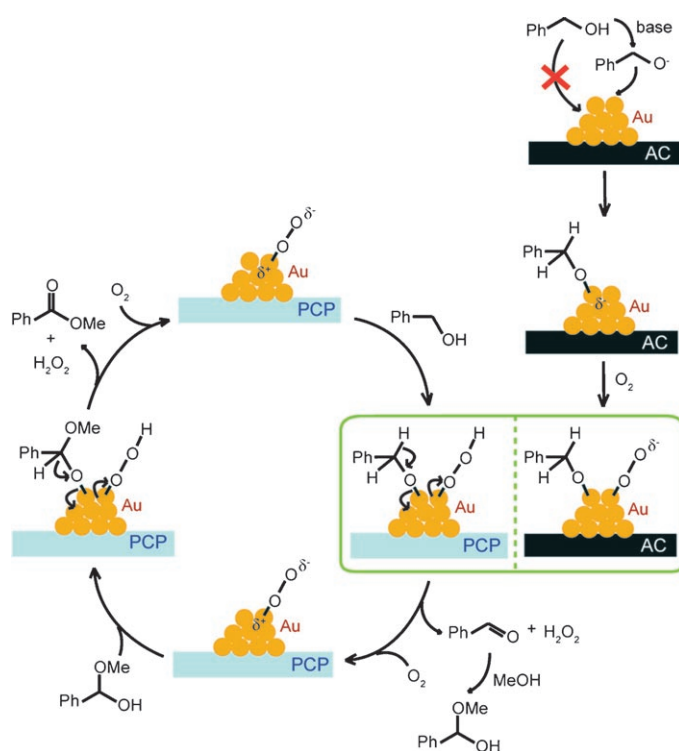
[a] Reaction conditions: 1 mmol benzyl alcohol, 0.5 mmol base, 99 mg 2 wt % Au catalyst (Au 1 mol %), 3 mL MeOH, 14 μL *n*-pentadecane, $p\text{O}_2$ 0.5 MPa, 80 °C. [b] SG: solid grinding, CVD: chemical vapour deposition. [c] GC yield by using *n*-pentadecane as an internal standard. [d] Only support (99 mg) was added. [e] 1 wt % Au catalyst (198 mg) was used.

erally the main product in the presence of base.^[2] In contrast, Au clusters on Cu-PCPs exhibited high selectivity towards benzaldehyde (entries 6–12). In alcohol oxidations, the addition of a base accelerates the reaction by deprotonation of the alcohol. However, Cu-PCPs were regarded as acidic supports by the measurement of the pH of Cu-PCPs dispersed in water. Therefore, weakly acidic Cu-PCP surfaces reduced the deprotonation of benzyl alcohol (step i in Scheme 1) and, in particular, formation of the hemiacetal intermediate (step ii). This would result in lower conversions than for neutral MOF-5 and Al-MIL53 surfaces, where benzaldehyde would be the main product. Another interesting feature is that Cu-PCPs were active as heterogeneous catalysts in the oxidation of benzyl alcohol without Au deposition (entries 6, 8, 11). However, catalytic activity was obviously enhanced by the incorporation of Au clusters.

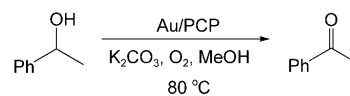
Secondly, the oxidation reaction also proceeded over Au/MOF-5 without base (entry 14). Gold clusters and NPs were successfully deposited directly onto acidic supports, such as AC and SiO₂, by SG with Me₂Au(acac) followed by the reduction of Au^{III} to Au⁰ with H₂ or calcination,^[22] however, over Au/AC^[3d] and Au/SiO₂ the yields were extremely low without base (entries 15, 16). Rossi and co-workers proposed a reaction mechanism for the oxidation of glucose over Au/AC that the Au surfaces deposited on AC could not adsorb alcohol and base was requisite to form the alcoholate before the adsorption onto Au. Then, oxygen could adsorb onto the Au^{δ-} sites^[23] (Scheme 2) because anionic Au clusters are considered to be favourable for the activation of oxygen molecule on the Au surfaces.^[24] Concerning the structure of oxygen adsorbed, calculations by density functional theory (DFT) have suggested that oxygen molecule may adsorb perpendicularly onto gold clusters.^[24] In contrast, the surfaces of Au clusters on PCPs were sufficiently active to adsorb alcohol to form Au–alcoholate without base or were negatively charged to adsorb oxygen (Scheme 2). This implies that the PCP might electronically affect Au clusters, whereas AC did not. Although SG method could directly deposit small Au clusters onto both of AC and SiO₂ as well as PCP, PCP supports are advantageous in the base-free alcohol oxidation.

Catalytic activity order of Au/PCPs in the oxidation of 1-phenylethanol was almost similar to that the oxidation of benzyl alcohol (Scheme 3 and Table 2). Moreover, Au/MOF-5 (entry 1) exhibited the highest catalytic activity among all the Au catalysts including Au/AC (entry 4).

In summary, the SG method using Me₂Au(acac) as an Au precursor was proved to be the simplest and the most efficient method to deposit Au clusters directly onto PCPs. The SG method can be applied not only to PCPs but also to other materials, especially, acidic supports such as SiO₂, WO₃, and AC on which Au NPs can not be directly deposited by the conventional deposition–precipitation method. In addition, SG needs neither organic solvents nor careful washing after the vapour deposition of Me₂Au(acac). Gold clusters and NPs on PCPs exhibited noticeably high catalytic activity in liquid phase alcohol oxidation even in the ab-



Scheme 2. Plausible pathways for benzyl alcohol oxidation over Au/PCPs and Au/AC.



Scheme 3. Oxidation of 1-phenylethanol.

Table 2. Oxidation of 1-phenylethanol catalyzed by Au/PCPs (SG).^[a]

Run	Catalyst ^[b]	Yield [%] ^[c]
1	Au/MOF-5	79
2	Au/MIL-53	56
3	Au/CPL-2	13
4	Au/AC	77

[a] Reaction conditions: 1 mmol 1-phenylethanol, 0.5 mmol K₂CO₃, 1 mol % [Au], 3 mL MeOH, pO₂ 0.5 MPa, 80 °C, 23 h. [b] 2 wt % Au catalysts were prepared by SG. [c] GC yield of acetophenone by using *n*-pentadecane as an internal standard.

sence of base and showed unique product selectivity which can be tuned by the selection of PCP supports, in particular, by the degree of surface acidity, for benzyl alcohol oxidation.

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