Gold-Platinum Bimetallic Clusters for Aerobic Oxidation of Alcohols in Aqueous Media Open to Air at Room Temperature under Base-Free Conditions

Hiroyuki Miyamura, Ryosuke Matsubara, and Shū Kobayashi*

Department of Chemistry, School of Science and Graduate School of Pharmaceutical Sciences, the University of Tokyo, The HFRE Division, ERATO, Japan Science Technology Agency (JST), Hongo, Bunkyo-ku, Tokyo 110-0033, Japan

Electronic Supplementary Information

1. General: Tetramethylsilane ($\delta = 0$) was used as an internal standard for ^{1}H NMR and $CDCl_3$ ($\delta = 77.0$) for ^{13}C NMR. The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in literature. ICP analysis was performed on Shimadzu ICPS-7510 equipment. GC analysis was performed on Shimadzu GC-17A apparatus (column = J & W SCIENTIFIC DB-1 for primary alcohols and GL Science TCWAX for secondary alcohols). The structures of the known compounds were confirmed by comparison with commercially available compounds or literature data. TEM, STEM and EDS images were obtained using a JEOL JEM-2100F instrument. All TEM specimens were prepared by placing a drop of the solution on carbon-coated Cu grids and allowed to dry in air (without staining).

2. Preparation of PI Pt/Au

2-1. Preparation of co-polymer:

Co-polymer was prepared along the method shown in reference 6.

2-2. Preparation of PI Pt/Au: Copolymer (800.0 mg) and $NaBH_4$ (50 mg) were dissolved in diglyme (13 mL) at room temperature, to this solution was slowly added a mixture of chloro triphenylphosphine gold (I) (31.8 mg) and sodium hexachloro platinum (VI) (34.8 mg) with 4 mL of diglyme. The mixture was stirred for 16 h at room temperature and diethylether (80 mL) was slowly added to the mixture at room temperature. Brown coaservates enveloped the metal dispersed in the medium. The catalyst capsules were then washed with diethylether several times and dried at room temperature. Next, the catalyst capsules were heated at 150 ˚C for 5 h without solvent to prepare brown solid, which was washed with dichloromethane and water then grinded by pestle and mortar. Resulting powder was heated at 170 ˚C for 5 h without solvent to afford PI Pt/Au (625.9 mg). 10-20 mg of PI Pt/Au was heated in mixture of sulfuric acid and nitric acid at 200 ˚C for 3 h, the mixture was cooled to room temperature and aqua regia was added. The amount of gold in the resulting solution was measured by ICP analysis to determine the loading of gold and platinum. (Loading Au: 0.073 mmol/g, Pt: 0.076 mmol/g)

2-3. Preparation of PI Ni/Au (from $Ni(OAc)_2$): The preparation method was same as PI Pt/Au but the Nickel diacetate was used instead of sodium hexachloro platinum (VI).

2-4. Preparation of PI Ni/Au (from $NiCl_2(PPh_3)_2$): The preparation method was same as PI Pt/Au but the Dichloro bistriphenylphosphine nickel was used instead of sodium hexachloro platinum (VI).

2-5. Preparation of PI Ag/Au: The preparation method was same as PI Pt/Au but the Silver benzoate was used instead of sodium hexachloro platinum (VI).

2-6. Preparation of PI Ir/Au: The preparation method was same as PI Pt/Au but the Hydrogen tristriphenylphosphine iridium was used instead of sodium hexachloro platinum (VI).

2-7. Preparation of PI Pd/Au: The preparation method was same as PI Pt/Au but the Palladium acetate was used instead of sodium hexachloro platinum (VI).

2-8. Preparation of PI Au: Copolymer **1** (800.0 mg) and $NaBH_4$ (10.1 mg) were dissolved in diglyme (13 mL) at room temperature, to this solution was slowly added chloro triphenylphosphine gold (I) (31.1 mg) with 3 mL of diglyme then the solution turned wine red. The mixture was stirred for 3 h at room temperature and diethylether (30 mL) was slowly added to the mixture at room temperature. Brown coaservates enveloped the metal dispersed in the medium. The catalyst capsules were then washed with diethylether several times and dried at room. Next, the catalyst capsules were heated at 150 ˚C for 5 h without solvent to prepare wine red solid. Thus prepared solid was washed with dichloromethane and water, crashed and dried to afford wine red powder. This powder was heated at 150 ˚C for 5 h without solvent to afford PI-Au **3**. 20-30 mg of PI-Au **3** was heated in mixture of sulfuric acid and nitric acid at 200 ˚C for 3 h, the mixture was cooled to room temperature and aqua regia was added. The amount of gold in the resulting solution was measured by ICP analysis to determine the loading of gold.

2-9. Preparation of PI Pd: The preparation method was same as PI Au but the Palladium acetate was used instead of chloro triphenylphosphine gold (I).

2-10. Preparation of PI Pt: The preparation method was same as PI Au but the sodium hexachloro platinum (VI) was used instead of chloro triphenylphosphine gold (I).

3. Oxidation of alcohols catalyzed by PI Metal catalysts

3-1. A typical procedure for aerobic oxidation of alcohols catalyzed by PI Pt/Au in BTF/water: *Sec*-phenetyl alcohol (30.5 mg, 0.25 mmol), PI Pt/Au (Au loading: 0.073 mmol/g, 1 mol% based on Au), water (1.5 mL), and benzotrifluoride (1.5 mL) were combined in a round-bottomed flask. After the mixture was for 5 h under O_2 atmosphere at room temperature, the catalyst was collected by filtration and washed with diethylether and water. The aqueous layer was washed with diethylether (20 mL). The yield was determined by GC analysis with reference to an internal standard (IS = anisole).

3-2. Recovery and reuse of PI Pt/Au: Collected catalyst after the reaction as shown in 3-1 was dried *in vacuo* and heated 170 ˚C for 5 h under atmospheric hydrogen. Then the catalyst was used for next reaction.

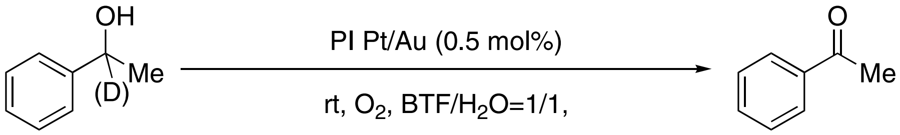
3-3. Aerobic oxidation of *sec*-phenetyl alcohol in water open to air at room temperature: *Sec*-phenetyl alcohol (30.5 mg, 0.25 mmol), PI Pt/Au (Au loading: 0.073 mmol/g, Pt loading: 0.076 mmol/g, 3 mol% as Au) and water (1.5 mL) were combined in a round-bottomed flask. After the mixture was stirred for 5 h open to air at room temperature, the catalyst was removed by filtration and washed with diethylether and water. The aqueous layer was washed with diethylether (20 mL), and the combined organics were concentrated under reduced pressure to afford analytically pure acetophenone.

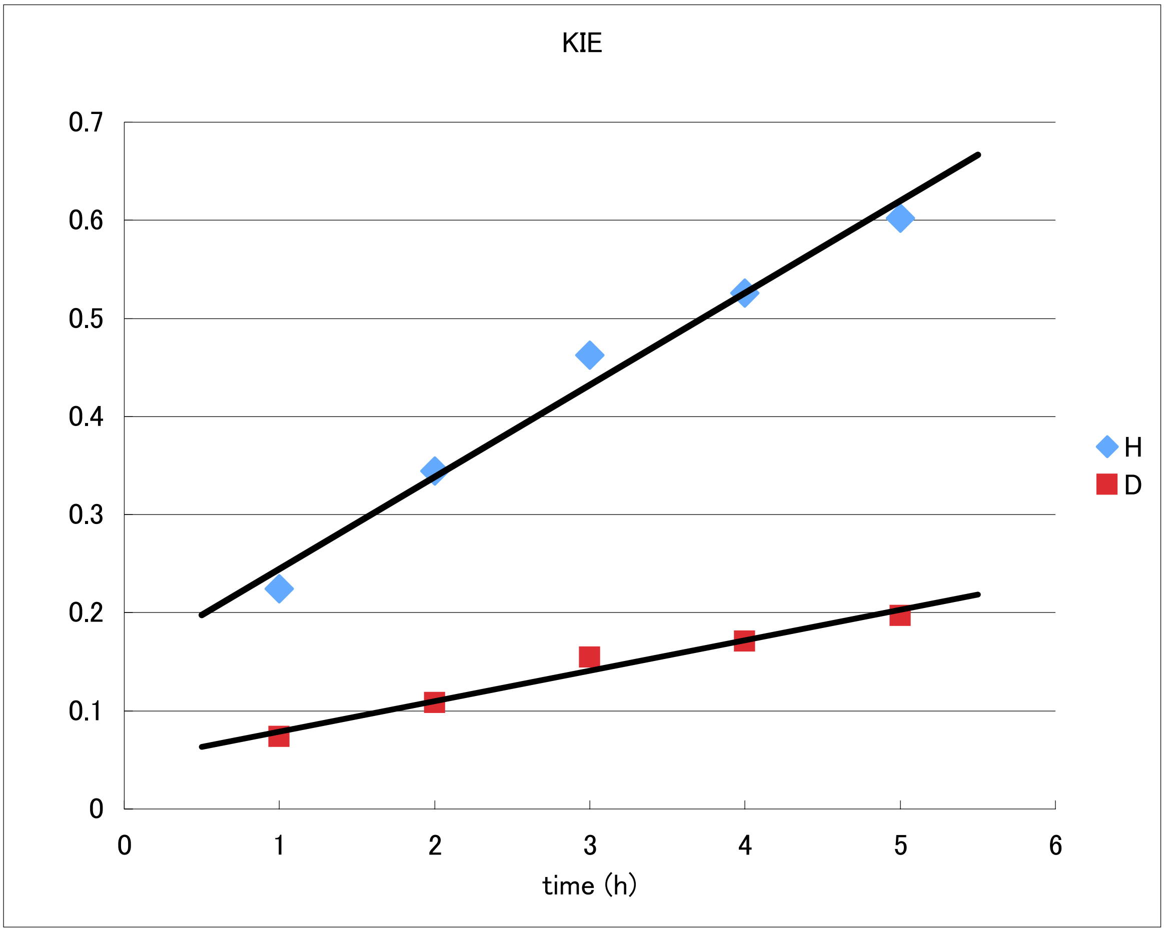
4. Kinetic isotope effect

4-1. Preparation of α deuterated *sec*-phenetyl alcohol: Sodium borodeutrate (1.0 g) was alowly added to the mixture of acetophenone (9.99 g) and methanol (13 mL) at 0 ˚C. The reaction mixture was stirred for 12 h at room temperature. The mixture was diluted with dichloromethane and saturated aqueous ammonium chloride was added to quench the reaction and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over sodium sulfate and the solvent was removed *in vacuo*. Pure α deuterated *sec*-phenetyl alcohol (8.88 g, 87% yield) was obtained after distillation.

4-2. Study of isotope effect: Substrate (*sec*-phenetyl alcohol or α deuterated *sec*-phenetyl alcohol) with 12 mL of BTF was added to the mixture of PI Pt/Au (Au loading: 0.049 mmol/g, Pt loading: 0.052 mmol/g) 102.3 mg in 12 mL of water. The mixture was stirred under atmospheric O_2 at room temperature and slight amount of organic layer (about 0.2 mL) was taken by a syringe to the GC analysis (SI_Scheme 1). Conversion was determined by the ratio of remaining starting material and product. The results were described in a plot of natural logarithm of 1/S (ratio of remaining substrate) vs. time (h) and the reaction rate was obtained as a slope of graph (*k*). k_H and k_D were 0.0938 and 0.0310 then k_H / k_D was 3.0 (SI_Figure 1).

SI_Scheme 1



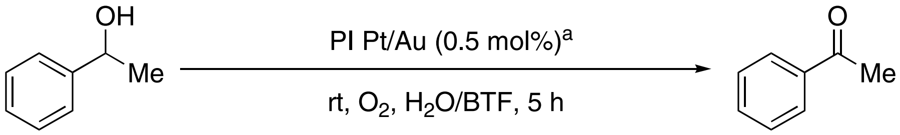


SI_Figure 1

5. Investigation of Reaction Media

5-1. Ratio of BTF and water: The reaction procedure was as same as 3-1 except the amount of catalyst and the solvent. While yield of product gradually decreased when the ratio of water was cut, the reaction proceeded even when 1/10 of water was used (SI_Table 1, entries 1-3). However, the reaction did not proceed at all without water (Entry 4). On the other hand, the reaction proceed without organic solvent.

SI_Table 1

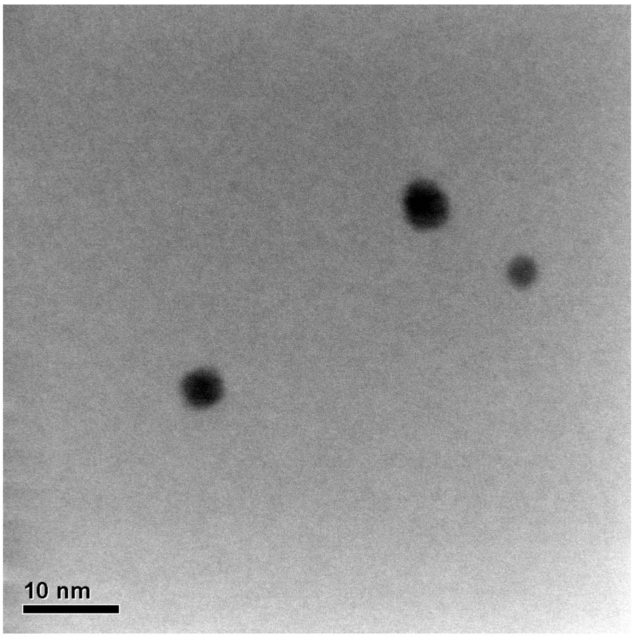


entry	BTF/H_2O (mL/mmol substrate)	yield (%)
1	6/6	59
2	6/2	50
3	6/0.6	42
4	6/0	trace
5	0/3	25[b]

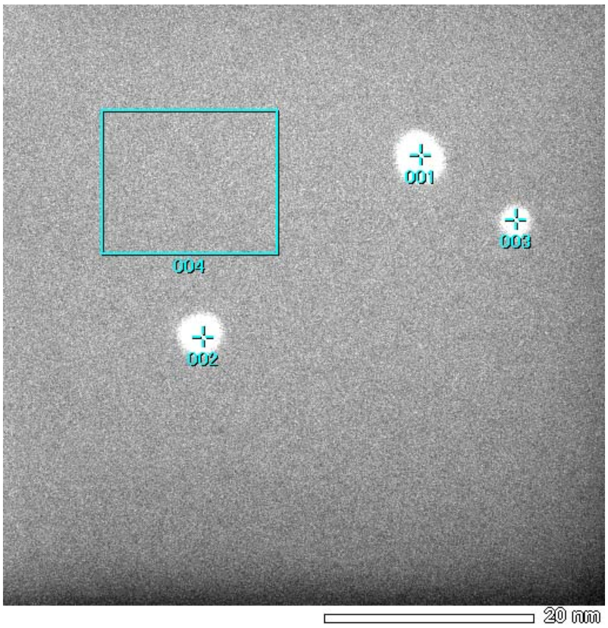
[a] Catalyst loading is based on Au. Ratio of Pt to Au is almost 1:1. [b] 0.1 mol% of PI Pt/Au for 3 h.

6. STEM and EDS analysis of PI Au, PI Pt/Au and PI Pd/Au.

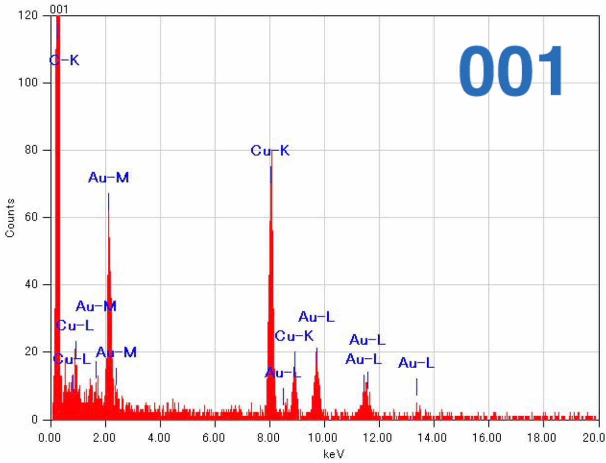
STEM and EDS analysis of PI Au, PI Pt/Au and PI Pd/Au were conducted. The size of clusters were distributed from 1.5 nm to 5 nm for all samples (SI_Figure 2, 8 and 13). The composition of each clusters was measured by EDS analysis. No peaks except the peak of cupper which is the material of grid were observed from the area without clusters (SI_Figure 7, 19 and 20). Peaks for gold were observed at the point on clusters in PI Au (SI_Figure 4-6). Peaks for both gold and palladium were observed at the point on clusters in PI Pd/Au (SI_Figure 10-12). Peaks for both gold and palladium were observed at the point on clusters in PI Pt/Au (SI_Figure 15-18). These result mean that the clusters in bimetallic catalysts are composed by both metals.



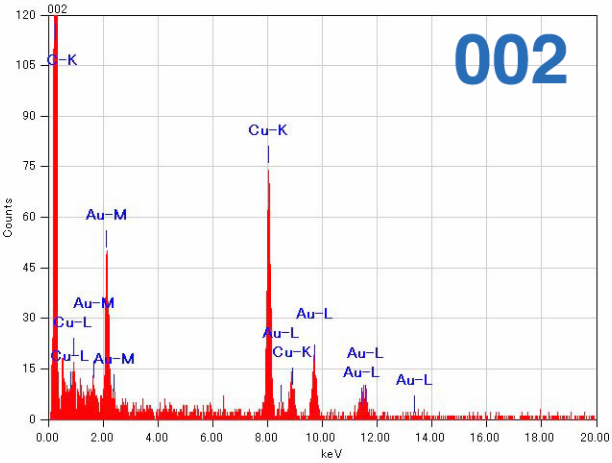
SI_Figure 2. STEM image of PI Au



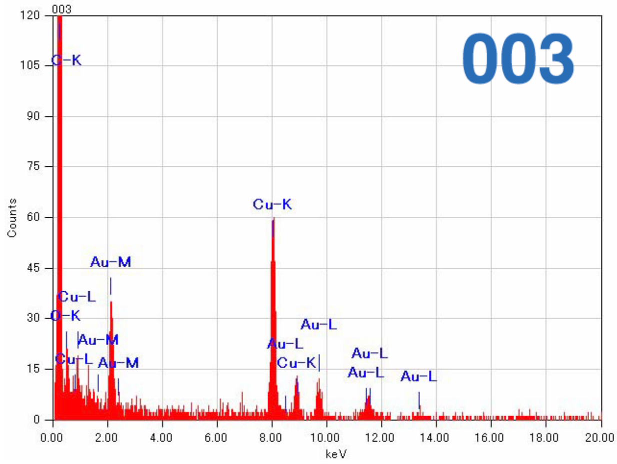
SI_Figure 3. Map of EDS point analysis in PI Au



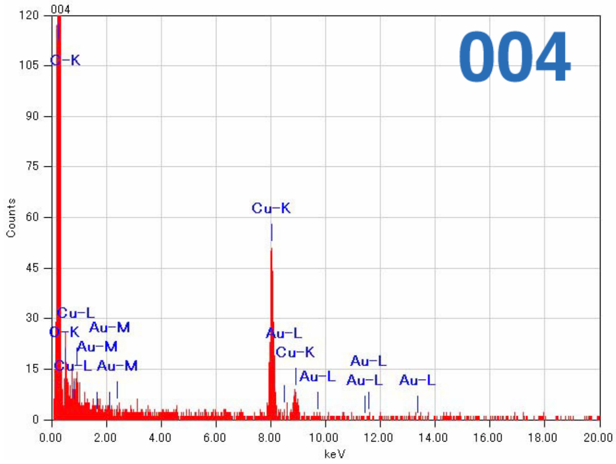
SI_Figure 4. EDS spectrum at point 001



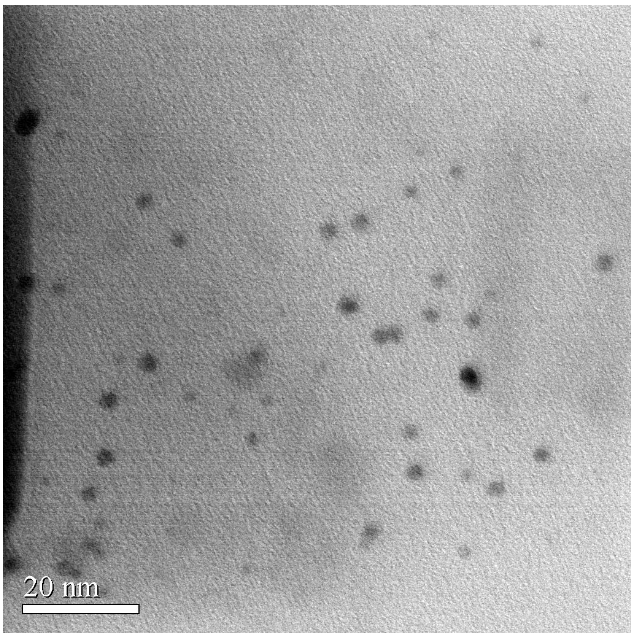
SI_Figure 5. EDS spectrum at point 002



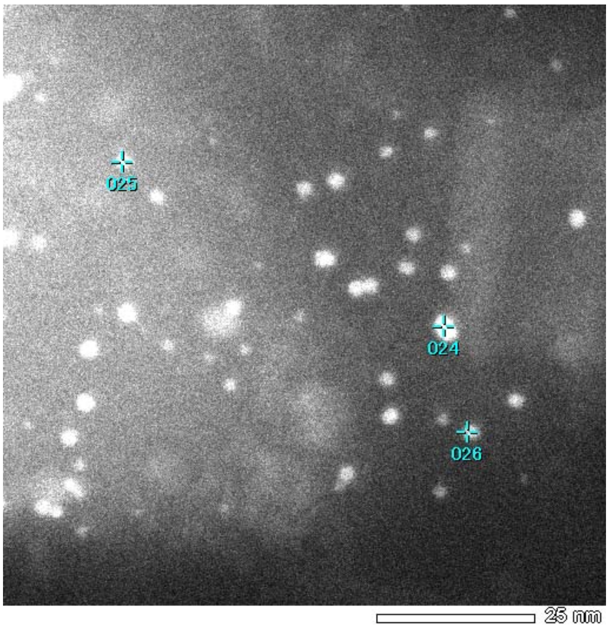
SI_Figure 6. EDS spectrum at point 003 (background)



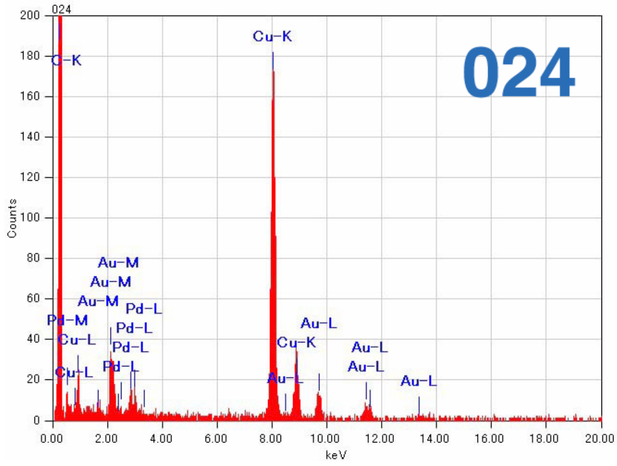
SI_Figure 7. EDS spectrum at area 004



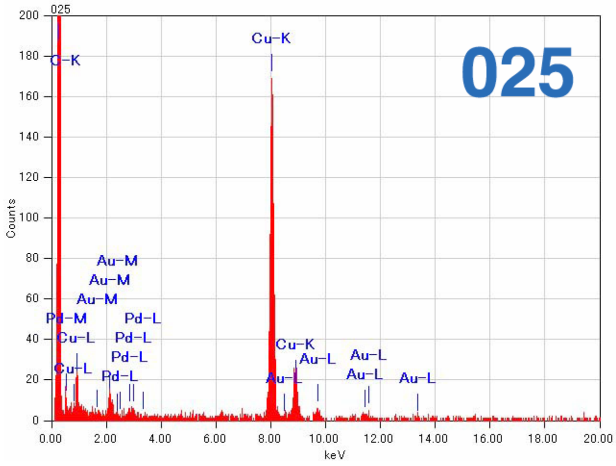
SI_Figure 8. STEM image of PI Pd/Au



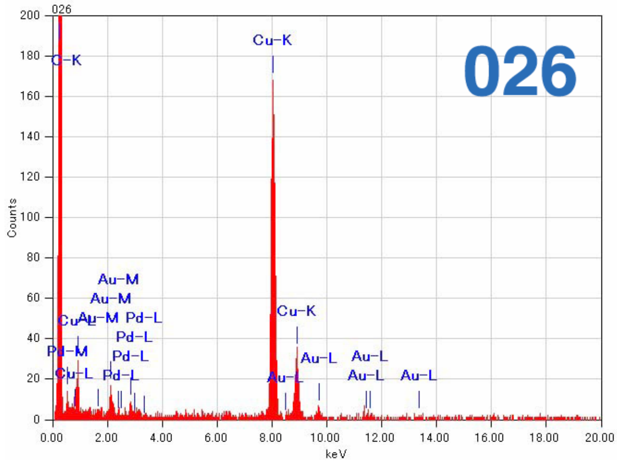
SI_Figure 9. Map of EDS point analysis in PI Pd/Au



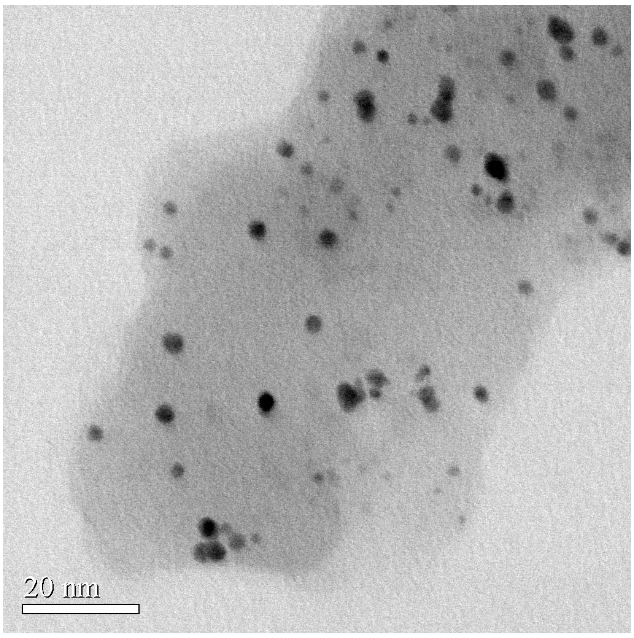
SI_Figure 10. EDS spectrum at point 024



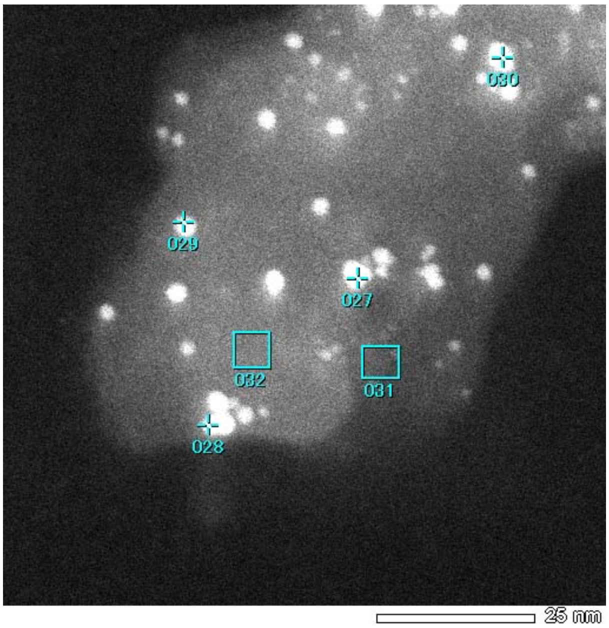
SI_Figure 11. EDS spectrum at point 025



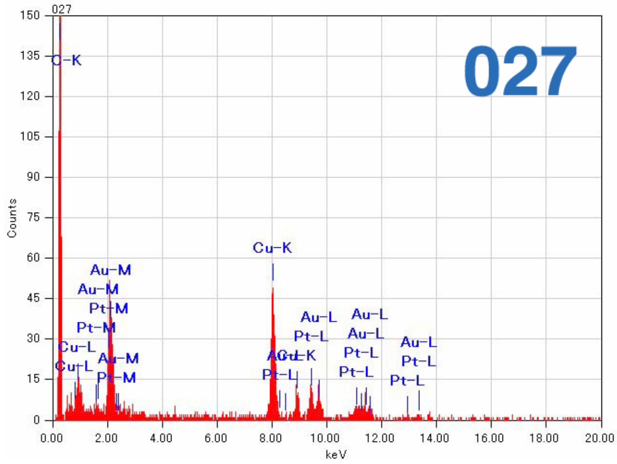
SI_Figure 12. EDS spectrum at point 026



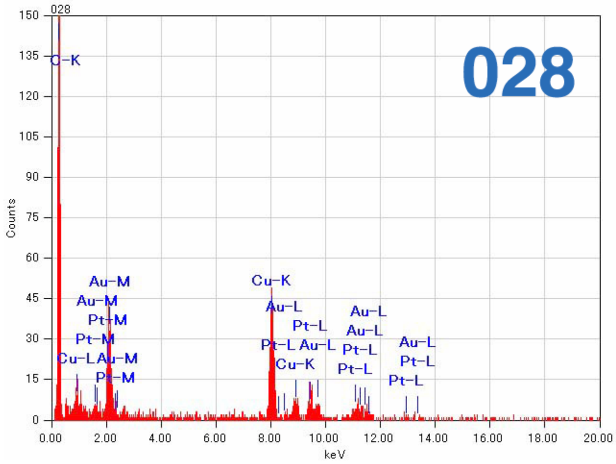
SI_Figure 13. STEM image of PI Pt/Au



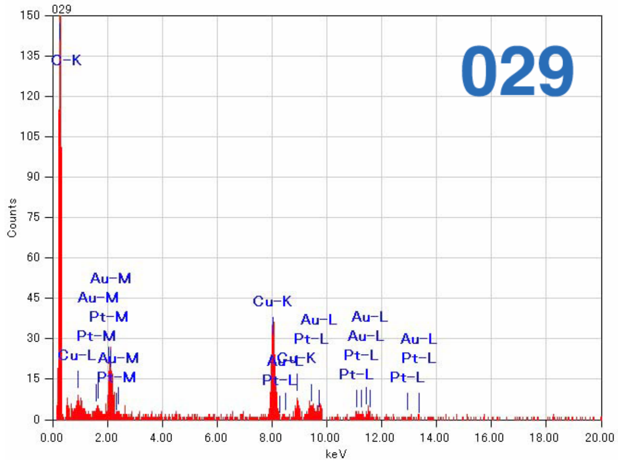
SI_Figure 14. Map of EDS point analysis in PI Pt/Au



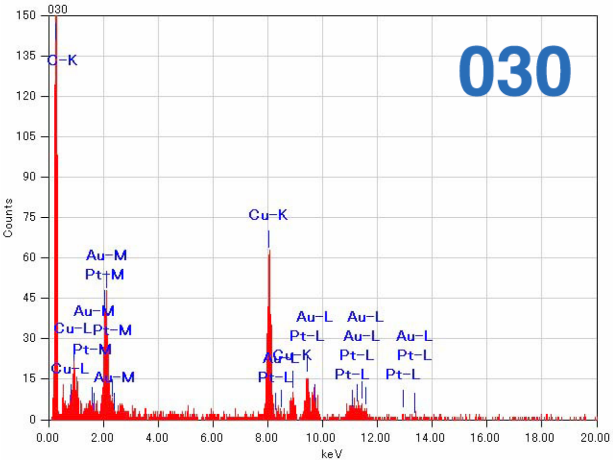
SI_Figure 15. EDS spectrum at point 027



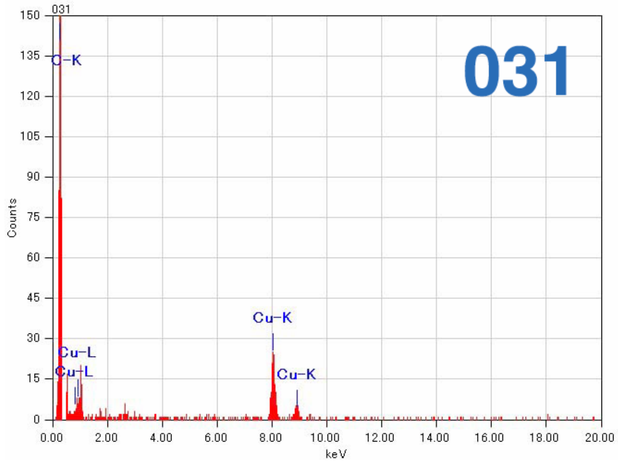
SI_Figure 16. EDS spectrum at point 028



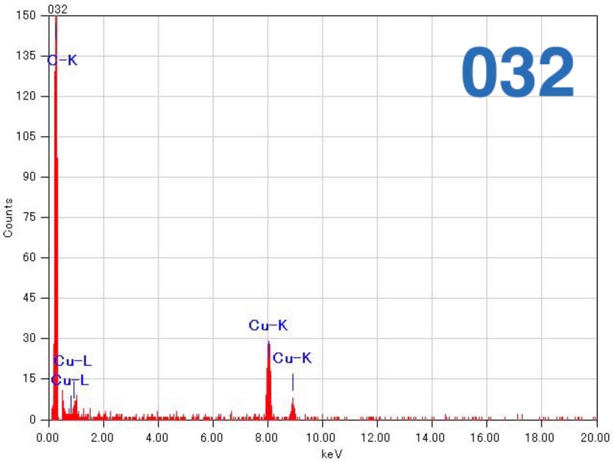
SI_Figure 17. EDS spectrum at point 029



SI_Figure 18. EDS spectrum at point 030



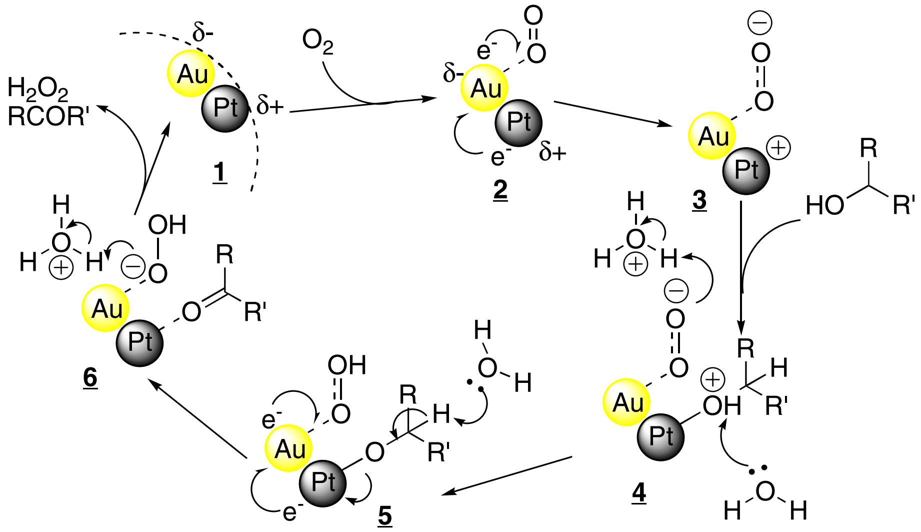
SI_Figure 19. EDS spectrum at area 031 (background)



SI_Figure 20. EDS spectrum at area 032 (background)

8. Reaction Mechanism.

Although extensive mechanistic study has not yet been conducted, an assumed mechanism of PI Pt/Au-catalyzed aerobic oxidation of alcohols is shown in SI_Figure 21. Adsorbed oxygen is activated at the site of the electron-rich gold atom by donating electrons from the metal (**2**, **3**). An alcohol coordinates to the electropositive Pt (**4**), followed by abstraction of the α-hydrogen by water and subsequent electron transfer to the oxygen through the metal (**5**). The carbonyl compound thus generated is finally eliminated from the metal surface, accompanied by hydrogen peroxide formation (**6**). Based on the isotope kinetic study ($k_H/k_D = 3.0$), the α-hydrogen abstraction should be involved in the rate determining step. Water was found to be indispensable for the reaction progress, which prompted us to suppose that water helped the abstraction of the α-hydrogen as a hydrogen transporter under hydrophobic polystyrene surroundings.



SI_Figure 21. A possible reaction Mechanism