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Electronic Supplementary Information for:

# Reactivities of Platinum Subnanocluster Catalysts for Oxidation Reaction of Alcohols.

*Masaki Takahashi,*[a] *Takane Imaoka*[b] *and Kimihisa Yamamoto**[b]

[a]*Graduate School Department of Interdisciplinary Research, University of Yamanashi, 4–4–37 Takeda, Kofu 400–8510.*

[b]*Chemical Resources Laboratory Tokyo Institute of Technology 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503 (Japan)*

*E-mail: yamamoto@res.titech.ac.jp*



## 1. Structure of TPM-DPA G4

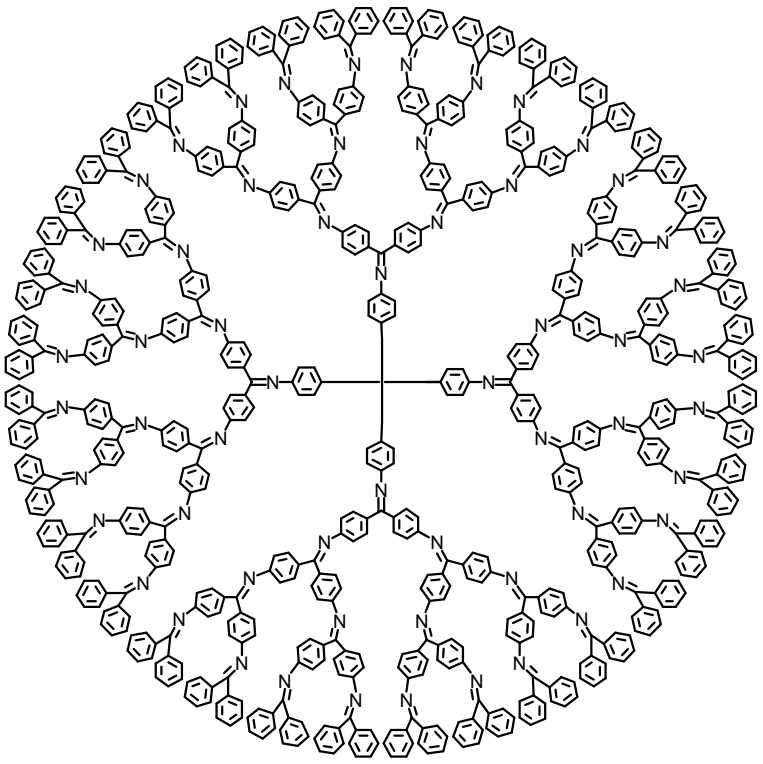

**Figure 1**. Molecular structure of TPM-DPA G4.

## 2. Materials and chemicals

TPM-DPA G4 was synthesized by a previously reported method.[1] Methanol of LC/MS grade, dehydrated acetonitrile of for organic synthesis, benzaldehyde of the grade for organic synthesis and anisole of the grade for organic synthesis were purchased from Kanto Chemical Co., Inc., and used without further purification. Dehydrated chloroform of the grade for organic synthesis was purchased from Wako Chemical Co., Inc., and used without further purification. 1-Phenylethanol was purchased from Tokyo Chemical Industry Co., Ltd., and used without further purification. Platinum(IV) chloride, the 175-nm purified mesoporous carbon (GMC), *p*-trifluoromethylbenzylalcohol, *p*-methoxybenzylalcohol, *tert*-butylhydroperoxide and sodium borohydride were purchased from Sigma-Aldrich Co., Inc., and used without further purification.

## 3. General methods

The $^1$H NMR spectra were measured by a Bruker AvanceIII 400 at 400 MHz. The $^1$H NMR chemical shifts were referenced to tetramethylsilane (TMS: 0.00 ppm) as the internal standard. The ICP-MS of the catalyst was measured by a Shimazu ICPS-8100. Stirring (700 rpm) of the oxidation reaction was done using a Zodiac, Personal Organic Synthesizer, CCX-3200 at 298 K. The XPS were measured by a Ulvac-Phi・ESCA1700R. The STEM (HAADF and bright field) images were obtained by a FE-TEM
instrument (JEM-2100F, JEOL) and a copper grid (Nisshin EM Co. Ltd.) was used in this measurement.

## 4. Experimental details

### Preparation of Pt clusters

**$Pt_{12}$@DPA G4/GMC**: All processes were conducted under a dry nitrogen atmosphere. A 985 μl solution (12 equivalents for the TPM-DPA G4) of $PtCl_4$ (3.44 mM) in acetonitrile was added to a 95.3 ml solution of DPA G4 (2.99 μM) in chloroform-acetonitrile (1:1) in a 200 ml flask in a glove box. After stirring for 30 min, 386 μl (61 equivalent relative to the platinum) of a sodium borohydride solution (0.53 M) in methanol was added to the solution. Just after the addition of the boronhydride, GMC (66 mg) was added to the solution of the reaction mixture of $Pt_{12}$@DPA G4 in chloroform-acetonitrile (1:1). After the suspension of $Pt_{12}$@DPA

G4/GMC was stirred for 30 min, the suspension was filtered using a hydrophilic membrane filter (Merck Millipore, JHWP04700) and the filtrate was added to the 102 ml methanol solution to wash the catalyst. After stirring for 30 min, the suspension was filtrated using a hydrophilic membrane filter again followed by drying under reduced pressure for 12 hours. The amount of the platinum in the catalyst powder was then determined by ICP-MS after 20 mg of the powder was dissolved in solution (mixture of 5 ml sulfuric acid, 1 ml hydrogen peroxide water and 4 ml nitric acid ) by a micro wave process (Perkin-Elmer. Co., Multiwave 3000) and the solution was diluted by demineralized pure water.

**ICP-MS elemental analysis of Pt clusters**

**Table 1**. The amount of Pt cluster on GMC

| Ptx/GMC | Pt (wt%, based on the weight of GMC) | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $Pt_{12}$ | 0.51 | 0.24 | 0.17 |
| $Pt_{28}$ | 0.63 | 0.52 | 0.48 |
| $Pt_{60}$ | 0.78 | 0.68 | 0.56 |

**Typical procedure for Pt catalyzed oxidation reactions**: 1.68 mg $Pt_{12}$@DPA G4/GMC powder was added to a flask. 1-Phenylethanol (66.2 mg, 0.55 mmol) and a 400 μl TBHP (2.2 mmol) solution were then added to the flask. Shortly after the reaction mixture was stirred for 6 h at 25 $^{o}$C under air and 700 rpm, anisole (205 μl, 0.044 mmol) as the internal standard in a decane solution (0.22 M) was added to the reaction flask. The reaction progress was then monitored by $^{1}$H NMR after 6 hours.

**5. XPS of platinum clusters supported on GMC**

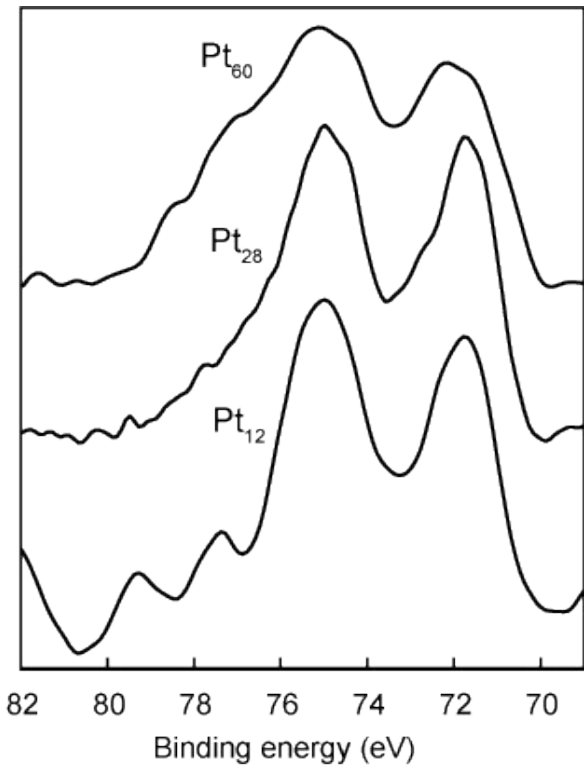


**Figure 2**. XPS of $Pt_{12}$, $Pt_{28}$ and $Pt_{60}$@TPM G4/GMC.

**6. Calculation of percentage of surface atoms of clusters**

| Number of atoms in cluster | $M_{13}$ | $M_{55}$ | $M_{147}$ | $M_{309}$ | $M_{561}$ |
|---|---|---|---|---|---|
| Percentage of surface atoms | 92 | 76 | 63 | 52 | 45 |

**Figure 3**. Full-shell magic number formation showing how the percent of atoms in a cluster present on the surface.[2]

Based on the percentage surfaces atoms of magic number clusters, a logarithmic function is determined using a method of least squares. From this function, the percentages of surface atoms of $Pt_{28}$ and $Pt_{60}$ were 85% and 75% respectively.

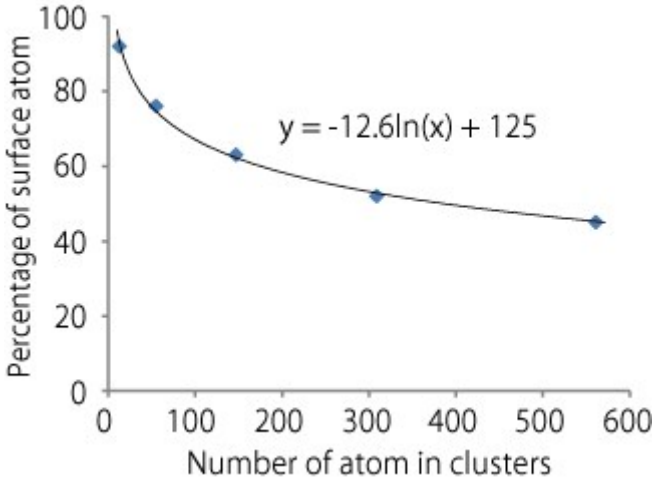


**Figure 4**. The graph and the logarithmic function of a percentage of surface atoms of the clusters.

**7. Reference**

1) O. Enoki, H. Katoh, K. Yamamoto, *Org. Lett*., **2006**, *8*, 569.

2) J.P. Wilcoxon, B.L. Abrams, *Chem. Soc. Rev*., **2006**, *35*, 1162.