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Reactivities of Platinum Subnanocluster Catalysts for Oxidation Reaction of Alcohols

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Atomicity-precise platinum subnanocluster (0.5-2 nm) catalysts were applied to the oxidation reaction of benzylalcohol with *tert*-buthylhydroperoxide (TBHP) as the oxidant. The subnanoclusters (SNCs) exhibited higher catalytic activities than the commercially available platinum nanoparticle catalysts. A size-dependence of the catalytic activities exhibited a volcano-shaped behavior in these oxidation reactions.

Introduction

Metal nanoparticles (2-10 nm) have been applied to catalysts for various oxidation reactions due to their high surface-to-volume ratios and size-specific reactivities.[1-4] Especially, metal subnanoclusters (SNCs, 0.5-2 nm) have drawn much attention in recent years because the properties of the SNCs drastically change with respect to the adsorption strength of the reactants on the under-coordinated surface atoms.[5-7] For instance, Vajda and coworkers showed that the Pt_{8-10} SNCs are 40–100 times more active for the oxidative dehydrogenation of propane than past catalysts.[8] Except for such a limited example, the size-dependence of the catalytic activities on a subnanometer scale has not yet been revealed because of the difficulty in the atomicity-controlled synthesis together with the effective suppression from aggregation.[6] To the best of our knowledge, no systematic studies on the size effect of one-atom controlled platinum SNC catalysts have been reported for the alcohol oxidation reactions.

We have developed a novel synthetic method of platinum SNCs employing a dendrimer reactor, which was designed to control the exact number of metal precursors in a limited nanospace. Fourth generation dendritic polyphenylazomethines[9] undergo a stepwise complexation
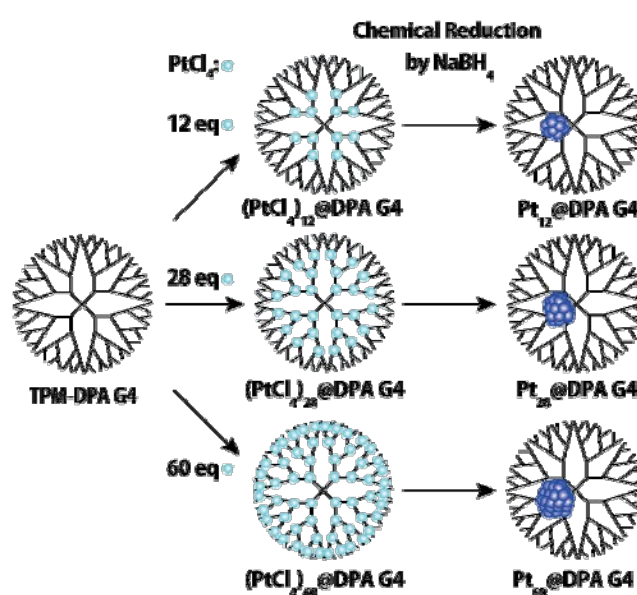

Figure 1. Preparations of platinum SNCs encapsulated by TPM-DPA G4.

with various metal chlorides.[10, 11] A dendritic phenylazomethine with a tetraphenylmethane core (TPM-DPAG4) has 4, 8, 16 and 32 imine sites on each layers of this molecule, and has the basicity gradient of its imine sites from the innermost layer to the outer layer. Based on this unique property, a dendrimer can define the number of accumulating metal chlorides especially at 12, 28 and 60 in the case of TPM-DPAG4. The stepwise complexation of TPM-DPAG4 with platinum(IV) chloride ($PtCl_4$) has been confirmed by the UV-vis spectroscopic titration displaying 4 independent isosbestic points that appeared in turn at 363.0 nm (0–4 equivalents), 366.5 nm (4–12 equivalents), 365.5 (12–28 equivalents) and 363.5 nm (28–60 equivalents).[11, 12] The stoichiometry required to shift the isosbestic points was consistent with the number of imine sites on each layer in the dendrimer, suggesting the stepwise radial complexation from the inner to outer imines. After equilibrating the metal complexations at the imine sites,

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Electronic Supplementary Information (ESI) available: Structure of TPM-DPA G4, Experimental section, calculated surface atom ratio of SNCs. See DOI: 10.1039/x0xx00000x

sodium borohydride was added to a solution of the dendrimer complexes affording the atomicity-precise metal clusters composed of 12, 28 and 60 platinum atoms (Fig. 1).[8] The dendrimer plays the two important roles: (1) defining the number of metal atoms, and (2) stabilizing the resulting SNCs from leaching and aggregation. We now report the synthesis of finely controlled platinum SNCs with a narrow size distribution, and the investigation of their catalytic activities for the oxidation reactions of alcohols.

Preparation and Characterization of Catalysts

The corresponding stoichiometric amount (12-, 28- or 60-equimolar amount to the dendrimer molecules) of 2.23 mM $PtCl_4$ in acetonitrile was added to a solution of TPM-DPAG4 in a mixed solvent (chloroform/acetonitrile = 1/1). After stirring for one hour for equilibration, sodium borohydride ($NaBH_4$) in methanol was added to the complexes to reduce the platinum(IV) chloride to zero-valent platinum within the dendrimer similar to the previously reported method.[11] The platinum SNCs encapsulated in the dendrimer were supported onto a graphitized mesoporous carbon (GMC) to suppress their post-aggregation.[13] After the stirring of the supported catalyst for one hour, the SNCs supported on GMC were filtered using a hydrophilic membrane filter (0.2 μm) followed by washing with methanol to remove the ionic boron-, sodium- and chlorine-containing impurities. These GMC-supported SNCs were characterized by HAADF-STEM and XPS analyses. The HAADF-STEM images of Pt_{12}, Pt_{28}, Pt_{60} SNCs and commercially-available platinum catalyst supported on activated carbon (6.9 wt% from Sigma-Aldrich Co.) are shown in Figure 1. These images indicate that Pt_{12}, Pt_{28} and Pt_{60} have narrow size distribution in diameter (Fig. 2). A previous study has shown the monodispersity of the as-synthesized Pt_{12} clusters by ESI-TOF-MS[7, 11] suggesting the possible size control at the atomic level. The XPS of the Pt_{12}, Pt_{28} and Pt_{60} $4f_{7/2}$ binding energies were 71.8, 71.7 and 71.7 eV, respectively. By comparing these values with the bulk platinum $4f_{7/2}$ (71.0 eV) and platinum(II) oxide (72.4 eV), it was confirmed that these precursor metals were successfully reduced to Pt(0) from Pt(IV). The ICP-MS elemental analysis of the catalyst was conducted to confirm the proper amount of platinum metals on the carbon support (see supporting information).

Procedures for Oxidation of Alcohol

To reveal the relationship between the size of the clusters and the catalytic activities, 1-phenylethanol was selected as a model substrate. 1-Phenylethanol (0.55 mmol) as the substrate, a 4-equimolar amount of *tert*-butyl hydroperoxide (TBHP) in a decane solution (5.5 M) as the oxidant and a platinum catalyst (0.016 mol%) were added to a reaction flask followed by stirring for six hours at 25 °C under air. The reaction progress of the oxidation reaction was determined by a ^1H NMR analysis by comparing the α-methyl proton signal (2.59 ppm) of the carbonyl group on the products with the methoxy proton signal (3.75 ppm) of anisole as the internal standard. To identify the catalytically-active species, various reaction conditions were studied.
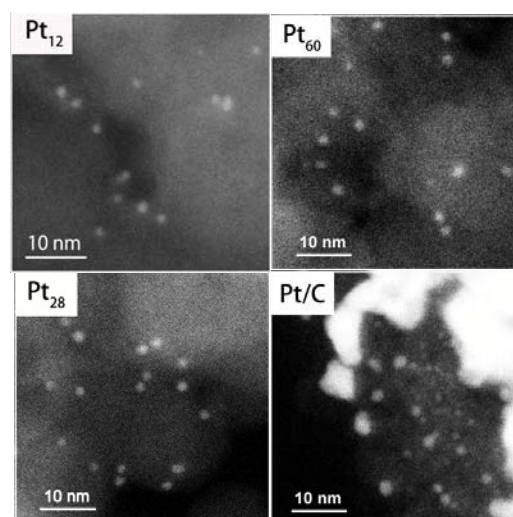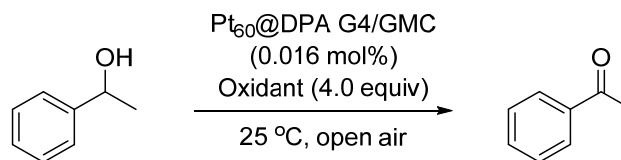

Figure 2. HAADF-STEM images of Pt_{12}, Pt_{28}, Pt_{60} and Pt/C (6. wt%).

Table 1. Control experiments of platinum cluster on GMC for oxidation reactions.

Entry	Conditions	TOF [Pt total atom^{-1} · h^{-1}]
1	Without oxidant	trace
2	Without catalyst	3
3	TBHP as oxidant	97
4	Filtrate using membrane filter	4

The reaction did not proceed at all without the oxidant or platinum catalyst (Table 1, Entries 1 and 2). After the oxidation reaction, the filtered solution was collected through a hydrophilic membrane filter (0.2 μm) to remove the platinum catalyst supported on GMC. This filtrate solution was again subjected to the oxidation reaction. However, the TOF value was very low. The HAADF-STEM images of the collected catalyst after the oxidation reaction did not show any change in the sizes of the platinum SNCs. These results indicate that the catalytically active species are the supported platinum SNCs on the GMC, but not the dissolved ionic or complex species.

Mechanistic Study of Alcohol Oxidation

Experiments to determine the rate-limiting step were conducted using α-deuterio-1-phenylethanol. The TOF for the oxidation of 1-phenylethanol is more than 8 times higher than

that of α-deuterio-1-phenylethanol. Matsumura and co-workers reported a smaller difference in the TOF than that in our reaction system using Pt on an activated carbon catalyst for the alcohol oxidation. They concluded that the rate-determining step is the benzylic C-H bond cleavage.[14, 15] The significant primary isotopic effect in the present reactions also indicates that cleavage of the benzylic C-H bond is the rate-determining step for this alcohol oxidation.[16]

In addition, adding TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl, 1 mol%) as a radical scavenger, which is 62.5 times higher than the amounts of the platinum catalyst in molar ratio of platinum atom, to the reaction system decreased the turn-over frequency from 98 to 29 [Pt total atom^{-1} · h^{-1}] (Fig 3). On the other hand, previous reports about platinum-catalyzed alcohol oxidation reactions using dioxygen as the oxidant showed no changes in the TOF by adding a radical scavenger to the reaction system concluding that their catalytic reaction mechanism is via an ionic intermediate, and not a radical intermediate.[14] In our reaction system, partial inhibition by radical scavengers was observed. Therefore, our oxidation reaction using TBHP as an oxidant might involve a mechanism via a radical intermediate. The TOF values [Pt atom^{-1} · h^{-1}] using *p*-methoxybenzalcohol, benzylalcohol and *p*-trifluoromethylbenzalcohol as substrates were 86, 109, and 85, respectively (Fig 4). In this reaction, the electronic state of the alcohol did not affect the reaction rate. This fact also supports the idea that our oxidation reaction is based on a radical mechanism.[14]

Summarizing these results, the plausible mechanism of this reaction involves the following 4 steps.
1) Oxidative addition of platinum cluster to TBHP affords catalytically-active platinum species, the alcoholate intermediate (Scheme 1).[17]
2) Ligand exchange on the platinum cluster with an alcohol to eliminate H$_2$O.
3) Generation of a short-lived radical on α-carbon of the alcoholate intermediate by the decomposition of TBHP on the surface of platinum clusters resulting in cleavage of the α-C-H bond of the alcoholate intermediate.[18]
4) Elimination of a carbonyl compound to regenerate the reactive platinum SNCs.

Size Effect of Alcohol Oxidations

The size dependence of the platinum SNC catalysts was investigated using platinum SNCs composed of Pt$_{12}$, Pt$_{28}$ and Pt$_{60}$ on GMC and commercially-available platinum catalysts supported on the activated carbon (6.9 wt% Pt). Pt$_{28}$ showed the highest TOF [Pt total atom^{-1} · h^{-1}] for the oxidation of 1-phenylethanol among these four catalysts (Fig 5). In general, smaller clusters have higher surface-to-volume ratio to activate the substrate than larger clusters. Assuming a face-centered-cubic lattice or hexagonal close-packed structure model, every platinum atom of Pt$_{12}$ will appear on the surface. The ratios of surface atoms of Pt$_{12}$, Pt$_{28}$ and Pt$_{60}$ are 100%, 85% and 75%, respectively.[19] In contrast, the particle diameter of the commercial catalysts is 2–4 nm for each particle composed of approximately 300 atoms.
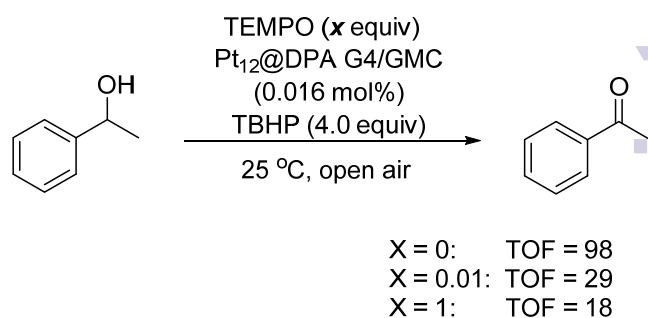

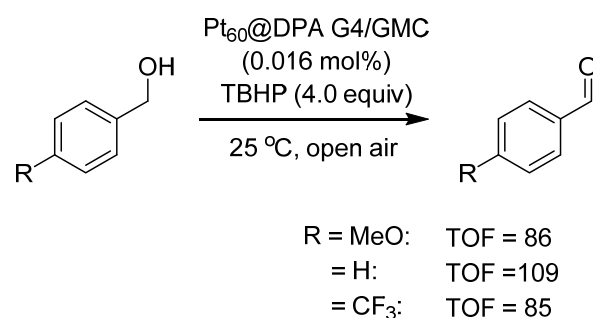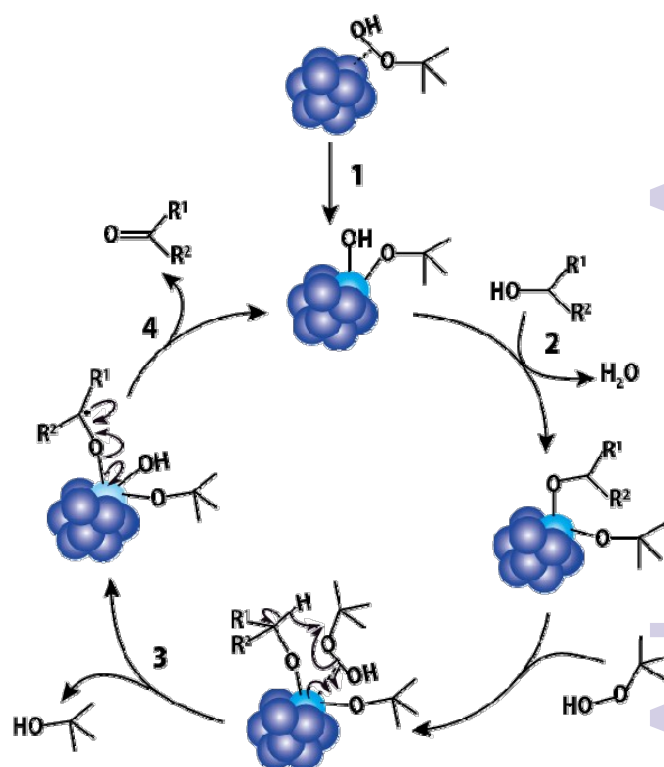**Figure 3**. Effect of TEMPO as radical scavenger in alcohol oxidations.

TEMPO (*x* equiv)
Pt$_{12}$@DPA G4/GMC
(0.016 mol%)
TBHP (4.0 equiv)
25 °C, open air

X = 0: TOF = 98
X = 0.01: TOF = 29
X = 1: TOF = 18

Figure 4. Effects of parasubstitution during oxidation of benzyl alcohols.

Pt$_{60}$@DPA G4/GMC
(0.016 mol%)
TBHP (4.0 equiv)
25 °C, open air

R = MeO: TOF = 86
= H: TOF = 109
= CF$_3$: TOF = 85

Scheme 1. Plausible mechanism of oxidation of alcohols to aldehydes and ketones.

In this case, about 30–50% of the atoms appear at the surface of the cluster. The TOF values [Pt surface atom^{-1} · h^{-1}] of Pt$_{12}$, Pt$_{28}$, Pt$_{60}$ and the commercial catalysts (6.9 wt%) are 0.93×10
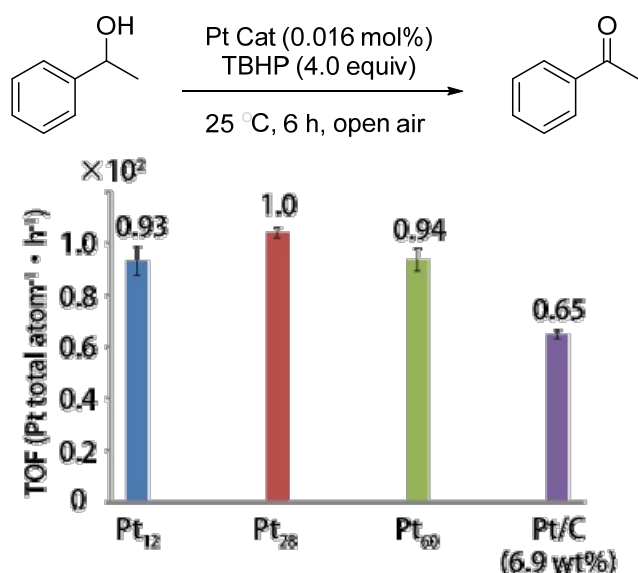
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Figure 5. Catalytic activities [Pt total atom^{-1} · h^{-1}] of oxidation reaction as a function of the number of platinum atoms.

$1.2×10^2$, $1.3×10^2$ and $1.6×10^2$ [Pt surface atom^{-1} · h^{-1}], respectively. Given these results, the surface-specific catalytic activities of the nanoparticles increase with the increasing particle size on the subnanometer scale. The volcanic behavior of the catalytic activities was not able to be explained only by the surface-to-volume ratio of the nanoparticles.[20] Concerning the unexpected decrease in the catalytic reactivity of the Pt$_{12}$ surface, it might be the strong absorption of an alcoholate intermediate resulting in a different transition state structure upon cleavage of the benzylic C-H bond on the under-coordinated surface atoms. However, the reason and mechanism are still not clear. Mechanistic investigation on these results are undergoing.

Conclusion

SNCs composed of 12, 28 and 60 platinum atoms (Pt$_{12}$, Pt$_{28}$ and Pt$_{60}$) were synthesized using TPM-DPAG4 as the template. These catalysts show higher catalytic activities than the commercially-available platinum catalyst. The size dependence of the alcohol oxidation catalyzed by platinum nanoparticles has a volcano-shaped behavior in the subnanometer region. These results show that the size-controlled synthesis of a metal catalyst is important in order to develop a new reactive catalyst for the alcohol oxidation reactions.
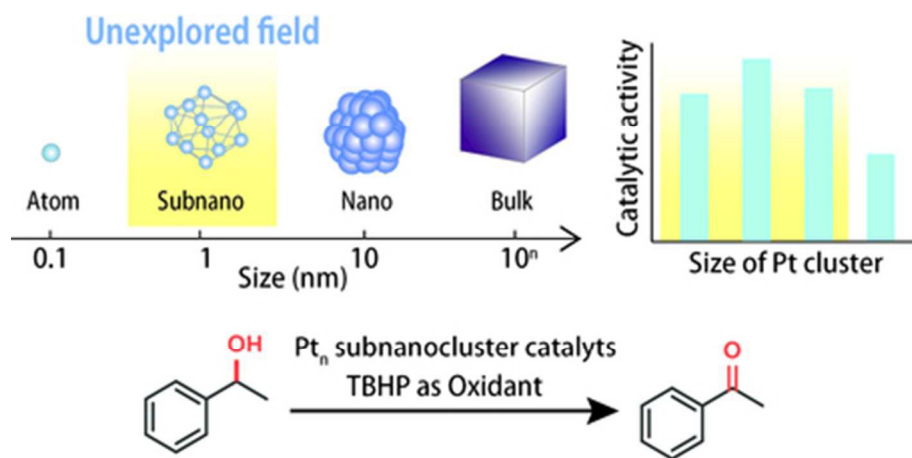
Notes and References

1. *Metal Nanoclusters in Catalysis and Materials Science: The Issue of Size Control*. B. Corain, G. Schmid and N. Toshima, Eds.; Elsevier: Amsterdam, **2007**.
2. S. Kobayashi and H. Miyamura, *Chem. Rec.* 2010, **10**, 271.
3. C. Jia, F. Schuth, *Phys. Chem. Chem. Phys.* 2011, **13**, 2457.
4. K. An, G. A. Somorjai, *ChemCatChem.* 2012, **4**, 1512.
5. A. Herzing, C. Kiely, J. Carley, P. Landon and G. Hutchings, *Science.* 2008, **321**, 1331.
6. A. Corma, P. Concepcio´n, M. Boronat, M. Sabater, J. Navas, M. Yacaman, E. Larios, A. Posadas, M. Lo´pez-Quintela, D. Buceta,
7. E. Mendoza, G. Guilera and A. Mayoral, *Nat. Chem.* 2013, **5**, 577.
8. T. Imaoka, H. Kitazawa, W.-J. Chun, S. Omura, K. Albrecht and K. Yamamoto, *J. Am. Chem. Soc.* 2013, **135**, 13089.
9. S. Vajda, M. J. Pellin, J. P. Greeley, C. L. Marshall, L. A. Curtiss, G. A. Ballentine, J. W. Elam, S. Catillon-Mucherie, P. C. Redfern, F. Mehmood and P. Zapol, *Nat. Mater.* 2009, **8**, 213.
10. Please see a molecular structure of TPM-DPA G4 in supporting information.
11. O. Enoki, H. Katoh and K. Yamamoto, *Org. Lett.* 2006, **8**, 569.
12. K. Yamamoto, T. Imaoka, W.-J. Chun, O. Enoki, H. Katoh, M. Takenaga and A. Sonoi, *Nat. Chem.* 2009, **1**, 397.
13. K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta and H. Chiba, *Nature.* 2002, **415**, 509.
14. M. Takahashi, T. Imaoka, Y. Hongo and K. Yamamoto, *Angew. Chem. Int. Ed.* 2013, **52**, 7419.
15. Y. Ng, S. Ikeda, Y. Morita, T. Harada, K. Ikeue and M. Matsumura, *J. Phys. Chem. C.* 2009, **113**, 12799.
16. K. Kon, S.M.A. Siddiki and K. Shimizu, *Journal of Catalysis.* 2013, **304**, 63.
17. Review of the primary isotope effect in organic reaction: E. Simmons, J. Hartwig, *Angew. Chem., Int. Ed.* 2012, **51**, 3066.
18. J-Q. Yu and E. J. Corey. *J. Am. Chem. Soc.* 2003, **125**, 3232.
19. H.R. Markus, A. Gansauer, *Radicals in Synthesis III.* Springer-Verlag Berlin Heidelberg. **2012**.
20. These ratios were calculated by comparing with surface atom number of magic number cluster. Please see supporting information.
21. Examples of volcano-shape catalytic activities in oxidation reactions with their particle sizes: (a) Y. Liu, H. Tsunoyama, T. Akita, S. Xie and T. Tsukuda, *ACS Catal.* 2011, **1**, 2. (b) N. An, S. Li, P. Wu, W. Zhang, J. Lee, S. Cheng, P. Zhang, M. Jia and W. Zhang, *J. Phys. Chem. C.* 2013, **117**, 21254.

The size-dependent catalytic activity for alcohol oxidation was investigated using the platinum subnanoclusters synthesized by the dendrimer template method.

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