

Atomicity-Precise Non-Magic Number Pt Clusters

Metal subnanoparticles composed of several tens of atoms are still unexplored materials despite their potential application for catalysis. The relationship between the atomic coordination structure and the catalytic activity at a one-atom resolution is very important in order to understand these materials. Recently, we have developed a dendrimer-based novel synthetic approach allowing precise control of the atomicity of these subnanoparticles. Because these ultrasmall particles are no longer periodic crystals but discrete molecular-like clusters, the available structural characterization method is limited. We describe how the structure and catalytic activity of these metal clusters are completely different from those of larger nanoparticles, and are quite sensitive to the atomicity.

Miniaturization of a nanoparticle catalyst is a reasonable way to improve its specific mass-catalytic activity by increasing the surface-to-volume ratio. However, it has long been considered that the limit of the size reduction is about 3 nm in the case of platinum particles although further improvement of the platinum-based fuel cell catalyst is strongly demanded. The reason for this limitation is usually explained by the stronger binding energy between the smaller platinum nanoparticle surface and oxygen molecules (atoms) that leads to a loss of surface-catalytic activity. Conventional nanoparticle synthesis can only control the average size (diameter) but not the exact number of the atomicity. Therefore, previous results for the effect of size on the activity just presented the average values of particles over a considerable atomicity distribution. Is every platinum subnanoparticle really inactive? To reveal this important relationship, we carried out the precise synthesis of Pt₁₂, Pt₂₈ and Pt₆₀ clusters, which can be synthesized with a phenylazomethine dendrimer as the template. The atomicities of these clusters deviate from the magic numbers, producing particularly stable clusters. To compare the magic number and non-magic number species, we also prepared Pt₁₃ using a specially designed phenyl-

azomethine dendrimer template (Fig. 1). A comparison of the catalytic activities and structural information between Pt₁₂ and Pt₁₃ can clarify the unknown properties of the non-magic number species.

Contrary to expectation, the smaller subnanoparticles (Pt₁₂, Pt₂₈ and Pt₆₀) are still active catalysts for the oxygen reduction reaction (ORR). In particular, the specific mass-activity of Pt₁₂ was ca. 13 times that of the commercially available Pt/C catalyst (3–5 nm diameter) [1]. A recent experiment demonstrated the surprising result that the catalytic activity of Pt₁₂ is ca. 2.5 times higher than that of Pt₁₃ despite the almost equivalent surface-to-volume ratio [2]. This result suggests that these clusters have a different atomic coordination or electronic structure. However, the standard experimental technique for nanoparticle characterization, such as TEM or XRD, was not suitable for determining this structural difference because the present clusters no longer have a periodic crystal structure and the atomicity difference is only 1. Instead, we measured the Pt-L₃ and -L₂ edge XAFS to reveal the local coordination structure together with the electronic structure such as the d-electron vacancy on the platinum atoms.

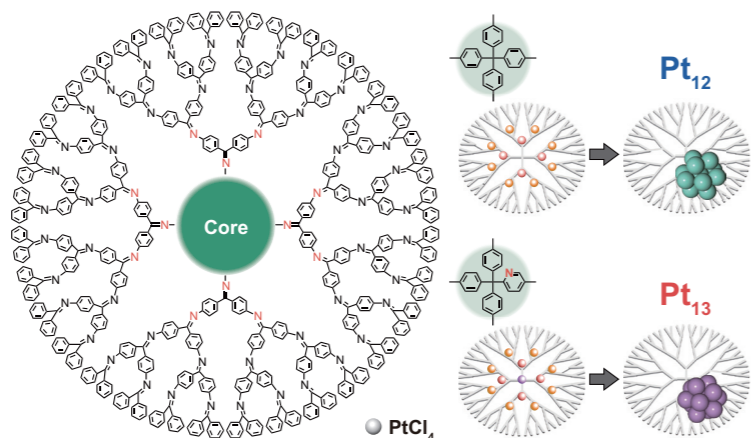


Figure 1: Dendrimer-based template synthesis of platinum subnanoparticles with precise atomicity control.

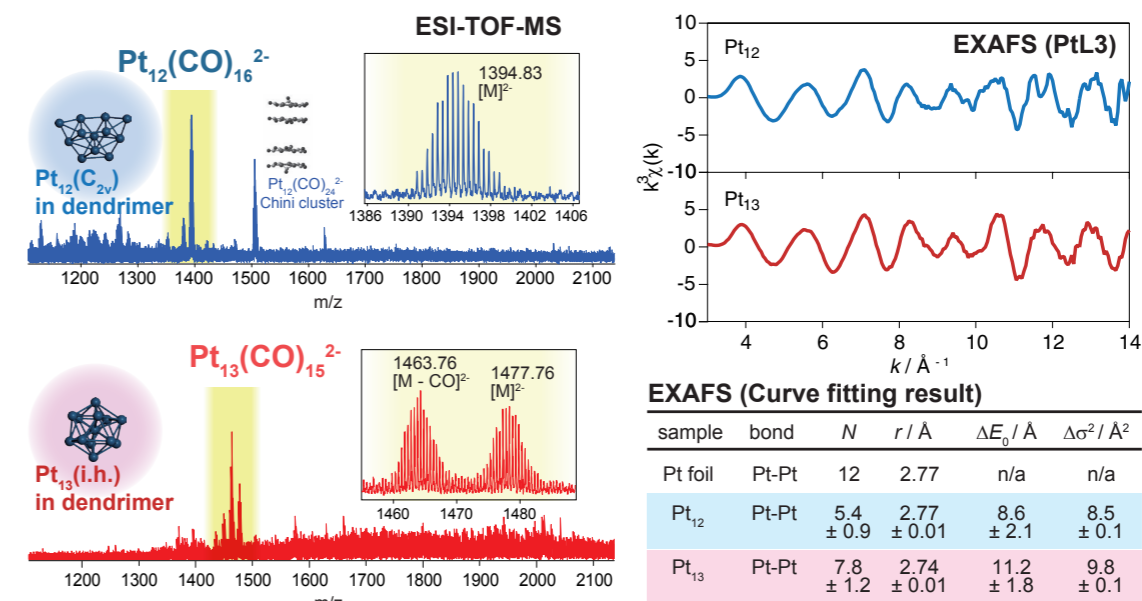


Figure 2: ESI-TOF-MS and Pt-L₃ EXAFS of Pt₁₂ and Pt₁₃ clusters.

The ESI-TOF-MS (electron-spray-ionization time-of-flight mass spectra) of Pt₁₂ and Pt₁₃ showed cluster ion peaks of each cluster consistent with the atomicity (Fig. 2). HAADF-STEM (high-angle annular-dark-field scanning transmission electron microscope) images demonstrated that they are ultra-small subnanoparticles (diameter: 0.9 nm). No diffractions by XRD suggested that they are not crystalline compounds. In spite of the significant difference in the ORR catalytic activity, no difference was observed in the XPS and XANES spectra (Pt-L₂ and -L₃). Beside the similarity of the two clusters, EXAFS showed a difference in the Pt-Pt coordination number (CN). Both clusters provided very small CN, which is consistent with the assumption of subnanoparticles. However, the CN of Pt₁₃ was clearly higher than that of Pt₁₂ (Fig. 2). This result suggests that these two clusters (Pt₁₂ and Pt₁₃) are basically different in their atomic coordination structure whereas their oxidation states are almost identical. The lower CN value of Pt₁₂ indicates a deformed and unsaturated structure. This finding is in line with the ESI-TOF-MS result that the observed Pt₁₂(CO)₁₆²⁻ cluster ion accompanies more carbonyl ligands relative to the Pt₁₃(CO)₁₅²⁻.

Cluster modeling calculations by the density functional theory (DFT) method also suggested a structural transition from Pt₁₃ to Pt₁₂. Several plausible structures were provided for Pt₁₃ and Pt₁₂. In combination with the XAFS and ESI-TOF-MS results, an icosahedral struc-

ture of Pt₁₃ and less symmetric C_{2v} structure of Pt₁₂ were supported. Based on the assumption of these structures, the difference in catalytic activity can be explained based on the oxygen binding energy on the cluster surfaces. Similar to the previously reported smaller platinum nanoparticles, the oxygen binding energy to Pt₁₃ is too strong for efficient ORR. On the contrary, the oxygen binding on Pt₁₂ is weaker and most suitable for ORR. The present observation suggests that the *fcc* structure of the Pt nanoparticle changes to an icosahedral-based structure around 1 nm, and finally becomes a less symmetric structure with a lower CN value below Pt₁₂. The catalytic activity no longer simply correlates to the size of the particles as expected based on common knowledge.

REFERENCES

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