Structural Analysis of Ultra-Small Metal or Alloy Clusters

By using XAFS, it is possible to structurally analyze ultra-fine metal particles (clusters) smaller than 1 nm supported on carbon or other solid-state materials at the atomic level, together with atomic resolution electron microscopy and elemental analysis. This is important for research on microscopic metal clusters which are expected to be used as highperformance catalysts.

Metallic clusters smaller than nanoparticles are expected to be used as catalysts in particular. Indeed, many reports have shown their excellent catalytic activity for molecular conversions [1]. Although both metal clusters and metal nanoparticles are aggregates of metal atoms, they have different scientific backgrounds. Nanoparticles are regarded as finely divided fragments of bulk metals, and so are in the category of solid-state physics, which is based on band theory. On the other hand, clusters are considered as a kind of molecule-like substance, which is based on molecular orbital theory. Despite this different categorization, the boundary is ambiguous. In this boundary region, the correlation between composition, structure and physicochemical properties is unclear. In particular, clusters composed of 10 to several tens of metal atoms are complicated to understand as a molecule, and yet are too small to be regarded as solids. Particles around 1 nm in diameter are remarkable substances as the proportion of their atoms that are surface atoms is almost 100%. However, there is no systematized theory, synthesis method, or structural analysis method at this frontier of material science.

Since metal clusters are extremely reactive compared to nanoparticles, most of them without ligand protection aggregate immediately in a solution, producing larger particles. Therefore, it is necessary to stabilize them on a solid-based support. Conventionally, only a gas phase method has been used to freely synthesize metal clusters with a definite number of atoms and composition. This gas phase method has extremely low synthesis throughput and still faces a major challenge for the practical application of catalysts. In contrast, we have developed a template synthesis method for metal clusters [2]. It is possible to control not only the particle

size of nanoparticles, but also the atomicity of metal clusters by using dendrimers or other multi-nuclear metal complexes as precursors. The next challenge is structural analysis of these subnanometer clusters. When the grain size becomes about 1 nm or smaller, structural analysis methods that can be used are limited, hindering extensive research of metal clusters. First, X-ray diffraction (XRD), which is commonly used for structural analysis of solid-state materials, is not available. As the crystal size becomes smaller, the width of the diffraction line widens, which makes the analysis difficult in principle. Another issue is a decrease in crystallinity. A 1-nm particle is composed of several tens of atoms, which is insufficient to make a rigid lattice. Therefore, the structure tends to be amorphous because the stable crystal structure no longer exists. It is very difficult to observe the clusters by using a conventional transmission electron microscope (TEM) due to the limit of resolution.

An aberration-corrected scanning transmission electron microscope (STEM) having atomic resolution is the optimal method to observe ultra-small particles (particle diameter and their dispersion). It is also possible to distinguish one heavy atom (metals) on a thick support material by using high-angle annular dark field (HAADF) imaging. It is possible to analyze what element the particle contains. Because the sensitivity of energy dispersive X-ray spectrometry (EDS) has become very high, the resolution of elemental mapping is now close to atomic resolution. Whereas STEM enables local analysis and observation of an outline, XAFS is a complementary analytical method allowing the average structure information to be obtained with subatomic resolution. It is the only method that can obtain information on the internal structure of subnanoparticles (Fig. 1).



Figure 1: Synthesis and observations of atom-precise and multi-metallic clusters with very small particle size. HAADF-STEM imaging allows atomic-resolution observations [3] and EDS mappings allow nanoscopic element characterization [4].



Figure 2: (a) The synthesis of Pt_a cluster from a platinum-thiolate complex. (b) k³-weighted Pt L₃ EXAFS and (c) the Fourier transform of the precursor complex and the Pt_a cluster

Table 1: Curve fitting results [4] of the EXAFS of Cu_{sp}Pt₁₆Au₁₂. The analysis suggested that Pt and Au are mixed, and Cu is separated as an oxide. M denotes Pt or Au.

Edge	Sample	Bond	N	r/Å	$\sigma^2 / 10^{-3} \text{ Å}^2$	$R_{\rm f}$ %
Cu K	Cu foil	Cu-Cu	12	2.55		
	$Cu_{32}Pt_{16}Au_{12}$	Cu-O	1.4±0.4	1.94±0.02	2.5±1.8	0.05
		Cu-M*	4.3±1.7	2.66±0.02	12.5±0.8	
Pt <i>L</i> ₃	Pt foil	Pt-Pt	12	2.77		
	Cu ₃₂ Pt ₁₆ Au ₁₂	Pt-M*	7.3±3.8	2.68±0.04	2.4±1.8	0.08
		Pt-Cu	2.8±1.5	(2.65)	12.5±0.8	
Au L ₃	Au foil	Au-Au	12	2.89		
	Cu ₃₂ Pt ₁₆ Au ₁₂ -	Au-M*	7.3±3.1	2.77±0.02	10.6±0.6	0.7
		Au-Cu	1.7±0.9	(2.66)	(12.5)	

* Though an ambiguity in the curve-fitting results originated from the poor EXAFS region (up to 9 Å⁻¹) of the Pt L_3 EXAFS spectra, we assumed that Pt and Au are a mixture but are not perfectly alloyed while Cu is separated as an oxide

The distance to the adjacent atoms can be obtained with sub-Å accuracy, and a deviation in the distance can also be known from the Debye-Waller factor. Also, the average particle diameter is roughly estimated from the coordination number (Fig. 2). For example, it has been found that the Pt - Pt bond distance of the Pt_a atom cluster is 2.71 Å, which is significantly shortened from 2.77 Å of the bulk Pt [3]. It is also observed that the Debye-Waller factor of the bond distance is very high, suggesting an irregular, amorphous structure.

In STEM-EDS, it is only possible to distinguish whether elements are compounded in particle units or not. In XAFS, when multiple metals are included, information on adjacent atoms as seen from each element is obtained and is essentially mixed, or separated states can be distinguished. For example, PtAuCu ternary cluster was confirmed to be mixed in STEM-EDS observation [4]. In this particle, it was proposed that Pt and Au are partially mixed while Cu is separated as an oxide, although an unambiguous coordination number of each element could not be well-characterized (Table 1). Such atomic level information is indispensable for exploring the origin of catalytic activity.

A new synthesis method and a new structural analysis method are necessary for new substance groups. XAFS is the only measurement method at present, which gives an average structure for each element regardless of the crystal structure, and is an indispensable tool for structural analysis of the subnano region. It is also suitable for in-situ analysis. Therefore, it is important to clarify the origin of its unique characteristics by determining changes in structure during catalyst operation.

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T. Imaoka^{1, 2, 3}, W.-J. Chun^{4, 3} and K. Yamamoto^{1, 3} (¹Tokyo Inst. of Tech., ²PRESTO-JST, ³ERATO-JST, ⁴International Christian Univ.)