Precise synthesis of 3d metal clusters and evaluation of their properties

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The metal clusters have attracted worldwide attention due to the unique reactivity and property beyond the extension of the bulk and nanoparticles. However, it has been technically difficult to systematically evaluate the property of various clusters since the synthesis method and the stable atomicity of clusters have been different for each element. To overcome this obstacle, we focused on the template method using a phenylazomethine dendrimer as a template molecule. This molecule has many imine sites which coordinate to metal ions and possesses a potential gradient of electronic density. Consequently, this dendrimer accumulates the regulated number of the metal salts and realizes synthesis of metal clusters with the finely controlled atomicity and elemental composition by chemical reduction of complexes.[1,2]

In this work, we focused on 3d metals which are relatively low-cost and abundant from Ti to Zn, and systematically evaluated the property of 3d metal clusters by unification of the synthesis method. We built the new liquid-phase reaction system using the same solvent and the counter anion of metal salts on the template method, leading to unification of the complexation behavior and synthesis condition for each cluster. In actual, we applied this system to 9 kinds of 3d metals and succeeded in the stepwise accumulation of each element into a dendrimer (Fig. 1A). The precise synthesis of 3d metal clusters with an atomicity of 28 was subsequently achieved by chemical reduction of these complexes. It was demonstrated that their clusters had the specific oxidation state peculiar to a cluster-size scale by UV-vis, XPS, and XAFS measurements. The reduction behavior of their clusters oxidized in air was also investigated through CO-TPR. Moreover, their clusters showed the unique reactivity as catalysts not found in conventional bulk metals over CO oxidation (Fig. 1B).

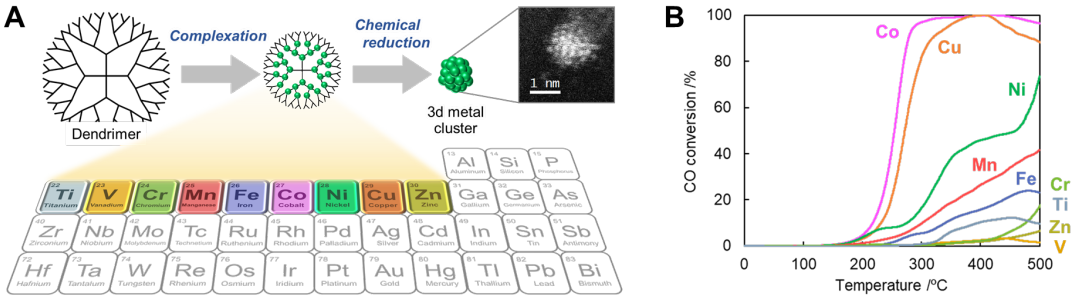

Fig. 1. (A) The schematic view of this work and a STEM image of Ni_{28} cluster. (B) Catalytic activity of 3d metal clusters with an atomicity of 28 over CO oxidation.

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