METAL NANOPARTICLES FOR CATALYSIS

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1. INTRODUCTION

Metal nanoparticles have attracted a great interest in scientific research and industrial applications, owing to their unique large surface-to-volume ratios and quantum-size effects.\(^1\)\(^-\)\(^3\) Since industrial catalysts usually work on the surface of metals, the metal nanoparticles, which possess much larger surface area per unit volume or weight of metal than the bulk metal, have been considered as promising materials for catalysis.

Industrial catalysts are usually composed of inorganic supports and metals on the supports. They are often prepared by heat treatment of metal ions on the support at high temperature sometimes under hydrogen. They have very complex structures. For example, they are the mixtures of metal particles with various sizes and shapes. Metal particles often strongly interact with the inorganic supports, thus resulting in the structure of half balls, for example.

In contrast, colloid chemistry has provided the colloidal dispersion of metal fine particles in water.\(^4\) In the 1950’s colloidal dispersions of metal fine particles were already prepared and applied to catalysis. Although they contained metal nanoparticles, the size of nanoparticles was not sufficiently monodispersed. In addition they were not stable enough when used in solution. Thus, there still remain many problems in the reproducibility of the preparation and catalysis of metal nanoparticles. In 1976, we prepared colloidal dispersions of rhodium nanoparticles protected by water-soluble polymers by reduction of rhodium(III) ions under mild conditions, i.e., reduction with refluxing alcohol in the presence of water-soluble polymers.\(^5\) These nanoparticles were applied as catalysts for hydrogenation of olefins. In 1989, we have developed colloidal dispersions of Pd/Pt bimetallic nanoparticles by simultaneous reduction of Pd and Pt ions in the presence of poly(N-vinyl-2-pyrrolidone) (PVP).\(^6\) These bimetallic nanoparticles display much higher catalytic activity than the corresponding monometallic nanoparticles, especially at particular molecular ratios of both elements. In this chapter, the preparation and catalytic properties of colloidal dispersions of metal nanoparticles will be discussed.

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Although there are many reports\textsuperscript{7,8} on the preparation of monodispersed metal nanoparticle catalysts supported on inorganic supports by physical methods, we have chosen not to include them in this chapter.

2. METALS AS CATALYSTS

Catalysts play a very important role not only in industrial chemical processes but also in chemical reactions (enzymatic reactions) in the human body. Industries usually use heterogeneous catalysts supported on inorganic supports at high temperature, and sometimes use homogenous catalysts at lower temperature. The former catalysts are much superior than the latter from the viewpoint of recycling of catalysts. In a human body or any living being, in contrast to industries, enzymes are used as catalysts in reactions at low temperature around 40 °C. They are very active and selective, and rather homogenous.

Both in industries and living beings, acid or base is used as the most popular catalyst for simple reactions, and metals work as active sites of the catalysts for rather complex reactions. Transition metals have often been used in the form of metal particles dispersed onto inorganic supports such as silica gel, alumina and activated charcoal. Dispersed particles on an inorganic support have advantages over metal powders in that:

(a) the particles can be readily dispersed through the use of the support;
(b) the resulting dispersed particles exhibit a much larger total surface area per unit weight than the bulk metal, thus allowing more effective utilization of the expensive transition metal as a result of dispersion;
(c) the active sites of the metal catalyst can be brought into a homogeneous condition by dispersion; and
(d) the small particles resulting from dispersion may exhibit new catalytic properties.

Colloidal dispersions of metal nanoparticles usually work at rather low temperature as homogeneous catalysts. In this point, metal nanoparticles are similar to enzymes and are often regarded as artificial enzymes.\textsuperscript{9} From the viewpoint of green chemistry (less energy, less byproduct, more efficiency, more selectivity, etc.), enzymes could be a model of industrial catalysts. Thus, metal nanoparticles could provide a step forward for industrial catalysts to step up from the present practical heterogeneous catalysts to more ideal and enzyme-like ones.

A polymer-protected metal nanoparticle catalyst has not only the similar advantages to dispersed particles on an inorganic support but also new benefits in that:

(a) colloidal dispersions can form “homogeneous” solutions;
(b) the protecting polymer can shield a nanoparticle catalyst from deactivation by catalytic poisons or air;
(c) the protecting polymer can interact attractively or repulsively with substrates, which results in high selectivity and/or sometimes high activity; and
(d) colloidal dispersions of metal nanoparticles transmit light more readily than powders.

As a result of this last benefit, colloidal dispersions of metal nanoparticles have frequently been used as catalysts in recent photochemical investigations.