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Aggregated structure analysis of polymer-protected platinum/ruthenium colloidal dispersions using EXAFS, HRTEM, and electron diffraction measurements

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Abstract

Polymer-protected platinum/ruthenium colloidal dispersions were prepared by refluxing mixed solutions of hexachloroplatinic(IV) acid and ruthenium(III) chloride in a mixture of ethanol/water (1/1 v/v) in the presence of poly(*N*-vinyl-2-pyrrolidone). The electronic spectra and transmission electron micrographs suggested that the colloidal dispersions are almost composed of the mixture of the small monometallic Pt and Ru clusters over all the ratio of Pt/Ru compositions. Extended X-ray absorption fine structure analyses and high resolution electron microprobe analyses indicated that no Pt/Ru alloy clusters exist in the dispersions, and the aggregation occurs between small monometallic Pt clusters (diameter ca. 15 Å) and partially oxidized Ru microclusters (diameter less than 10 Å). Electron diffraction measurements also suggested that the diffraction pattern of aggregated Pt/Ru cluster particles prepared by the simultaneous reduction of Pt and Ru ions is the same as that of the physical mixture of the small monometallic Pt and Ru clusters separately prepared. Therefore, it can be concluded that the aggregated Pt/Ru cluster particles, with 10 to 60 Å in diameter, are built up by small monometallic Pt clusters and partially oxidized Ru microclusters, and that Pt/Ru alloy clusters are not formed.

Keywords: Colloidal dispersions; Pt/Ru bimetallic clusters; Alloy; Aggregation; Coagulation; Agglomeration; Microclusters; EXAFS; Platinum; Ruthenium

1. Introduction

Many investigations have been carried out to interpret electronic structures closely related to catalytic properties, such as activity, selectivity, and stability for industrially important reactions on transition metal catalysts [1]. The electronic structure of small metal clusters and aggregates has played an important role in the chemical bonding and spectroscopic properties of such clusters. In particular, characterization of the electronic structure of small transition metal clusters and aggregates [2,3] has stimulated interest in better understanding of the active site of catalytic reactions on metal surfaces.

Homogenized transition metal catalysts such as polymer-protected metal clusters in colloidal dispersions, on which we have focused much attention in recent years, have represented the characters of the "naked" transition metal clusters because a strong metal–polymer interaction such as SMSI (strong metal–support interaction) is not generated. The naked transition metal clusters are anticipated as appropriate materials to investigate their surface electronic structures and geometries. In the study of cluster chemistry, naked metal clusters and aggregates are usually considered as typical models to resolve their electronic features from the theoretical and experimental approaches. Especially, naked metal clusters possessing up to 100 atoms are often employed in

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quantum chemical calculations to predict their electronic and magnetic properties, as well as their geometries [4]. Any representative calculations of the physical properties have to be started from special numbers such as $N = 13$, which is one of the "magic" numbers for metal clusters.

The concept of magic numbers is important to rationalize the geometries and electronic states of metal clusters systematically. The magic numbers $N = 13$, 55, 147, ... for cuboctahedral and icosahedral structures have been intensively studied. For instance, there has been controversy concerning the structure of high-nuclearity metal clusters. The two main structures are often described in the literature. One is a vertex-sharing icosahedral structure, which builds upon each unit, forming highly symmetric superclusters [5,6]. The other is a cubic close-packed (ccp) or hexagonal close-packed (hcp) structure with the outer geometry of a cuboctahedron [7,8].

Ligand-stabilized giant palladium clusters [9–11] (31.5 and 36.0 Å, reported by Schmid et al.) with an almost cuboctahedral shape were prepared from Pd(II) acetate in the presence of ligands, and characterized by means of HRTEM (high-resolution transmission electron microscopy) as well as XRD (X-ray powder diffraction). Bradley et al. [12–14] prepared palladium and platinum colloids of 7 and 1.3 nm mean diameter, respectively, in the presence of not only polymer but also of simple classical ligands like carbon monoxide and triphenylphosphine, and observed carbon monoxide adsorbed on colloidal particles by means of NMR techniques.

On the other hand, bimetallic clusters [15–19] and bulk alloys [20,21] have been extensively investigated with the aim of improving their preparative procedures as well as to control the activity and selectivity in catalysis. Especially, the additive effect of the second metallic component in bimetallic systems plays a significant role in the catalytic properties and electronic structures of bimetallic clusters, with respect to the practical [22–25] and theoretical [26–29] points of view. Henglein and co-workers [22,23] reported the formation process of gold–silver and gold–tin colloids prepared by γ-irradiation. Esumi and co-workers [24] studied the preparation and characterization of colloidal silver–platinum alloys obtained from the chemical reduction of silver(I) bis(oxalato)platinate(II). Bönnemann et al. [25] reported the hydrogenation activity of Pt/Rh bimetallic colloids supported on charcoal, which exhibits a maximum activity for crotonic acid at compositions of Pt/Rh = 1/4.

We have reported that the colloidal dispersions of bimetallic clusters, which can be prepared by refluxing alcoholic solutions containing two kinds of noble metal salts in the presence of poly(*N*-vinyl-2-pyrrolidone), exhibit a high degree of reproducibility in production and a high activity in catalysis, depending on the elemental compositions [30–34] and on the preparation method [35] of the clusters. The structures of Au/Pd [32], Pd/Pt [36], Pd/Rh [37], and Pt/Rh [38] bimetallic clusters in colloidal dispersions could be determined on the basis of EXAFS (extended X-ray absorption fine structure) and HRTEM. For the structures of Pd/Pt [36] and Pt/Rh [38] bimetallic clusters prepared under nitrogen, a core/shell model have been proposed. Moreover, we have found that the structure of Au/Pd bimetallic clusters [32], prepared by simultaneous reduction is composed of Au microclusters and Pd microclusters. We called this structure a "cluster-in-cluster" structure.

For the purpose of collecting the information on the relationship between the aggregated structure of clusters and their catalytic properties, Pt/Ru colloidal dispersions have been chosen because the combination of Pt atoms with Ru atoms might lead to the formation of Pt/Ru bimetallic clusters or Pt/Ru alloys, either of which is expected to appear some effective catalytic properties in activity and selectivity [33,34,39,40]. For instance, we have used Pt/Ru colloidal dispersions as catalysts for the visible light-sensitized reduction of carbon dioxide [41]. The catalytic activity was improved following air treatment of the Pt/Ru colloidal dispersions, as compared with monometallic colloidal dispersions.

In this paper we have studied the structural features, especially the aggregated structure of Pt/Ru colloidal dispersions by means of EXAFS, HRTEM, and electron diffraction measurements. A "Pt/Ru colloidal dispersion" is defined here as a dispersion of any kind of Pt/Ru composition, a "Pt/Ru bimetallic dispersion" is as a colloidal dispersion containing two kinds of monometallic clusters as well as bimetallic clusters, a "Pt/Ru bimetallic cluster" as a colloid in which two kinds of metal atoms are contained within a particle, and a "Pt/Ru alloy cluster" as a monocrystalline cluster in which two metal atoms are alloyed. We also propose new definitions about aggregation. Usually, "aggregation" is used as a general terminology indicating the aggregation process and "aggregates" is as the products of the aggregation process. In general, "coagulation" and "agglomeration" have a similar meaning in the sense of weaker interaction. In this paper, however, we define two kinds of terminology, "coagulation (coagulates)" and "agglomeration (agglomerates)," to express different features of aggregates. The former is used when the aggregates are formed by *strong* interaction between monocrystalline domain clusters. On the other hand, the latter is used when the aggregates are formed by *weak* interaction between monocrystalline domain clusters.

2. Experimental

2.1. Preparation of Pt/Ru colloidal dispersions

The Pt/Ru colloidal dispersions were prepared by the alcohol-reduction method [42,43]. Hexachloroplatinic(IV) acid (0.033 mmol) was dissolved in 25 ml of water, and ruthenium(III) chloride (0.033 mmol) was dissolved in 25 ml of ethanol. Poly(*N*-vinyl-2-pyrrolidone) (PVP, K-30, M.W. 40,000, 15.1 mg, 0.136 mmol of monomeric units) as a protecting polymer was added in an ethanol/water (1/1