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High-Resolution Electron Microscopy of Metal Clusters Supported on a New Type of Spinel Alumina

In the study of heterogeneous catalysis it is important to understand metal–support interaction at the interfaces between metal aggregates and oxide supports. By means of impregnation techniques using molecular metal cluster compounds it has become possible to prepare well-defined small homometal and/or alloy clusters fixed on the surface of inorganic metal oxides such as Al_2O_3, TiO_2, and SiO_2 (*1*). The catalytic activities are affected by the shapes of the metal aggregates and the degree of metal–support interaction, and these can be varied by the metal cluster nuclearity and the surface chemical properties of the oxide supports (*2*). Therefore, the sizes and shapes of cluster-compound-derived materials are at present being extensively investigated in terms of catalytic performances, e.g., activities and selectivities in typical reactions (*3*). Surface states and metal compositions of the oxide-supported cluster species are studied by means of *in situ* IR, XPS, and EXAFS (*1–4*).

As for a practical use of the metal clusters, one of the present authors (I.M.) studied olefin hydroformylation and CO-H_2 conversion catalyzed by Rh_4–Rh_{13} carbonyl clusters impregnated on suitable metal oxides such as MgO, La_2O_3, TiO_2, and ZrO_2 (*1, 4, 5*).

In contrast with the considerable accumulation of knowledge on the small metal clusters, not much attention has been paid to the role of the oxide supports. This may partly be due to the lack of information on the physical properties of the oxides. For example, γ-alumina, the most common oxide support, has irregular surfaces and porosity but only the apparent surface areas are used for characterization of the surface conditions. The microscopic surface structures of the oxides have not been studied, although according to some laboratory experiments the catalytic activities of the oxides are dependent on the type of crystalline surface represented by the Miller indices (*hkl*).

For the purposes mentioned above, an entirely new type of alumina, which is chemically, crystallographically, and morphologically well defined, has been prepared and utilized to investigate the morphologies of small metal clusters impregnated on the alumina. This communication reports on the direct observation of metal clusters supported on the alumina by means of a high-resolution transmission electron microscope. We emphasize that the new type of alumina, which is of spinel type and analogous to γ-alumina, is useful for the characterization of the metal clusters and their oxide supports.

The procedure of producing ultrafine particles of oxides such as Fe_2O_3, Al_2O_3, TiO_2, SiO_2, and MgO is based on the gas evaporation method which has been reported on briefly (*6*). Oxide particles with diameters between 50 and 800 Å are grown by heating a piece of metal in an atmosphere of oxygen and inert gases. The metal and gas purities were 99.99%, and the gas pressure was varied from several Torr up to 760 Torr. The pressure is varied for the type of oxides to be made. The metal was heated by means of an arc discharge between two metal elec-

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trodes. The oxide particles grow on direct oxidation of the metal vapor and/or on condensation of the oxide vapor in a completely dry vacuum pumping system. The gas evaporation method enables us to prepare extremely pure oxides up to 99.9999% purity. The purities are determined simply by the starting material used. Our gas evaporation chamber (1 m^3) is capable of producing the particles at the rate of about 5 g/h. The amount is sufficient for laboratory experiments on the catalyst.

The individual ultrafine particles of Al_2O_3 used in the present experiment are single crystals, and have almost spherical shapes. Three crystal structures for the alumina particles were found, called the δ'-, the θ_1-, and the θ_2-type. The first structure resembles the δ-type Al_2O_3. All of them are based on the spinel-type structure, and the cation vacancies and the tetrahedrally coordinated cations are arranged orderly in a perfect cubic arrangement for the oxygen atom (*6*). High-resolution microscopic observations revealed faceting and surface steps of the particles occurring on the atomic scale (*7*).

The apparent surface area of the Al_2O_3 particles are measured as 90 m^2/g according to the BET method. Therefore, as far as the surface area and the crystal structures are concerned, the alumina particles are almost comparable with those of the conventional γ-alumina gels for catalyst use.

The metal carbonyl cluster $Rh_6(CO)_{16}$ was synthesized after the procedure of Chini and Martinengo (*8*) and purified by several recrystallizations from CH_2Cl_2 solution. Following contact of $Rh_6(CO)_{16}$ (ca. 1 mg) in CH_2Cl_2 with the Al_2O_3 powder (ca. 8 mg), which was preevacuated at 350°C for 2 h, the $Rh_6(CO)_{16}$ was almost completely impregnated onto the alumina fine particles, and then the excess $Rh_6(CO)_{16}$ was removed by washing with some fresh solvent.

For the electron-microscopic observations the suspended fine particles impregnated with $Rh_6(CO)_{16}$ were sonicated at 25°C and then deposited on a copper grid covered with a holey carbon film. The specimen was subjected to evacuation in the treatment chamber of the electron microscope at 50–100°C for 15 min (10^{-5} Torr) to eliminate residual solvent, and then treated by further evacuation at 150°C and 10^{-7} Torr for 1 h. During these procedures the ancillary carbonyls of the impregnated clusters were possibly removed to provide naked Rh aggregates immobilized on the Al_2O_3 surfaces. This was implied by IR spectroscopic measurements which showed disappearance of the characteristic ligand carbonyls of $Rh_6(CO)_{16}$ at 2050 and 1800–1790 cm^{-1} by heating up to 150–200°C under evacuation at 10^{-5} Torr for 1 h. It was also interesting to find that the Al_2O_3 particles prepared by the gas evaporation method showed IR band intensities of surface OH groups at 3800–3700 cm^{-1} much weaker than those found with the conventional γ-alumina gel. This suggests that the surface OH groups on the Al_2O_3 particles are relatively few, similar to the case of a fully dehydrated γ-alumina gel.

The crystal orientation is controlled by monitoring convergent beam electron diffraction patterns. A precise alignment of a crystal is essential for high-resolution electron microscope observation. To conduct such a minute manipulation of fine particles on the side-entry type goniometer in the microscope, an Akashi EM-002A electron microscope operated at 120 kV was used in the present study. The microscope was operated easily by going back and forth between the microdiffraction mode and the high-resolution mode, which is the key point in high-resolution microscopy of individual small particles for the present catalyst research.

Figure 1 reproduces an electron micrograph of the spherical particles of the Al_2O_3 impregnated with $Rh_6(CO)_{16}$ clusters. Small speckles are distributed evenly on all particles. The speckles are measured to be less than 10 Å and can be individual Rh_6 clusters. They are recognizable most clearly on the particles which appear lighter in comparison to the darker ones. In such parti-

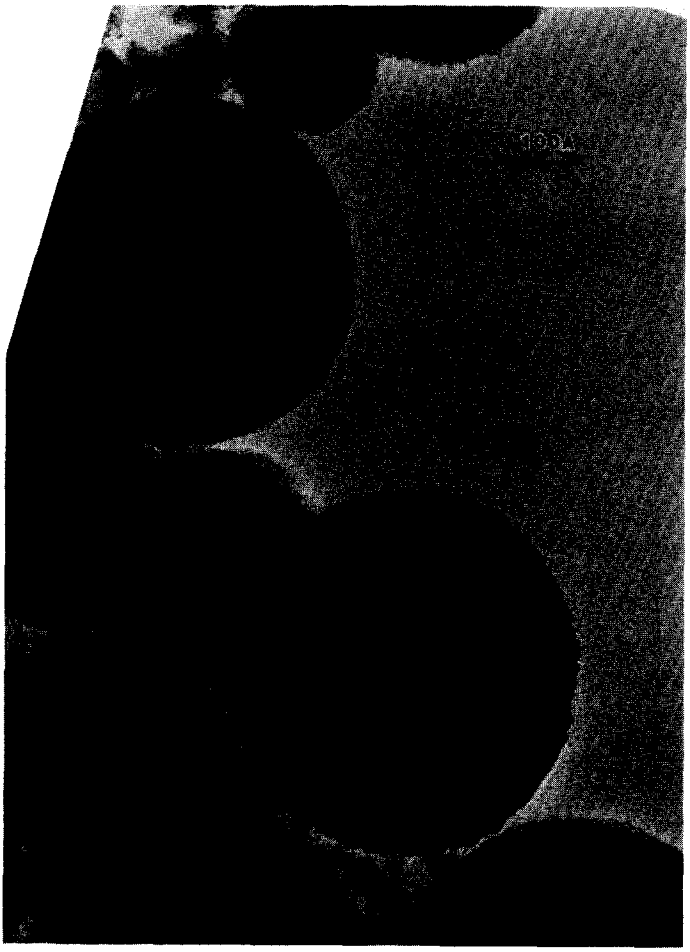

FIG. 1. Electron micrograph showing the spherical particles of a new type of spinel Al_2O_3. The particles were impregnated with $Rh_6(CO)_{16}$ clusters, which were imaged as fine speckles.

cles, less numbers of Bragg reflected waves are excited and thus the cluster images seem to be enhanced effectively. It should be emphasized also that the smooth surfaces of our Al_2O_3 particles are quite suitable for supporting small objects such as clusters because their image contrasts result predominantly from the phase contrasts. For conventional γ-Al_2O_3 supports, the imaging of the details of the small metal clusters might be prevented by the rough surfaces which are formed inherently during the dehydration process of aluminum hydroxides.

The particle which appears to be darker in contrast in Fig. 1 (indicated by an arrow) has been chosen and oriented with its $[1\bar{1}0]$ axis[1] perpendicular to the plane of the page. The electron diffraction pattern from the particle is assigned to its crystal structure as the θ_1-type Al_2O_3 (monoclinic; $B2/b$, $a = 11.1$, $b = 12.1$, $c = 17.7$ Å, $\beta = 103°$) (*6*). The particle is nearly spherical but after aligning the orientation its surface was found to be faceted. The faceting is seen in an enlarged image of the particle in Fig. 2. The predominant surfaces are the {111}-type planes which include the hexagonal net of oxygen atoms. However, it can be

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[1] The orientations and the Miller indices of the particles are represented, for simplicity, by those for the spinel structure.

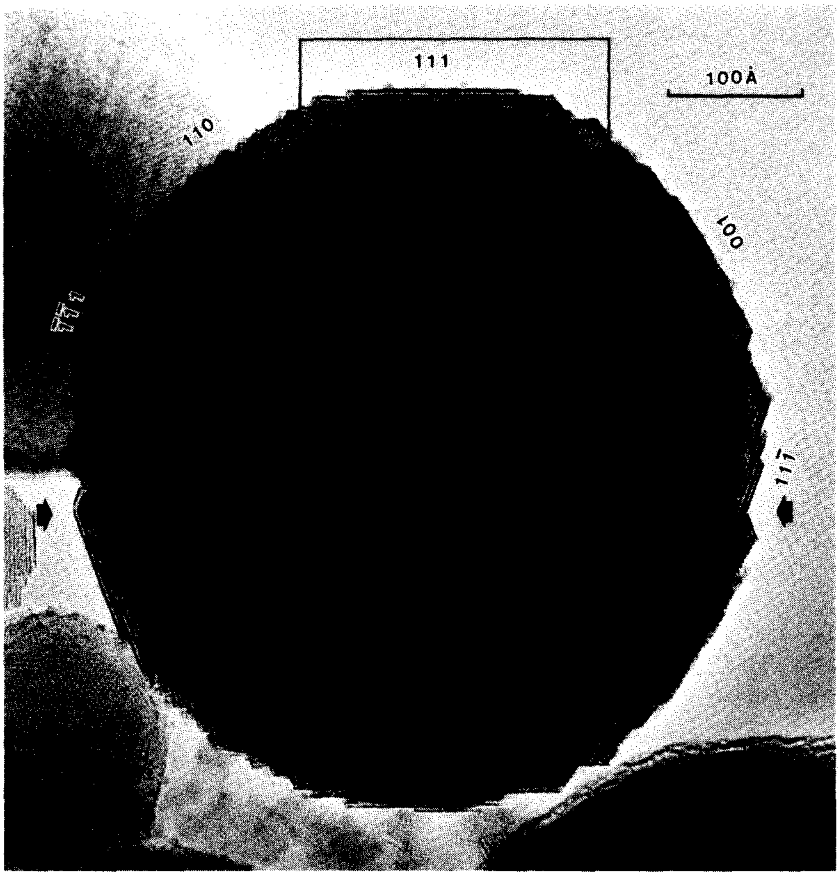

FIG. 2. Electron micrograph of the alumina particle marked by an arrow in Fig. 1. An exact alignment of the particle orientation in the $[1\bar{1}0]$ zone axis has revealed facetings which consist of the {111}- and the {100}-type surfaces. Two arrows indicate a (111) spinel twin plane.

expected that the terminating oxygen planes will be modified structurally because of the charge neutrality on the surfaces (*9*).

The fringe systems appearing throughout the particle are lattice fringes corresponding to d_{111} = 4.6 Å. The particle is twinned on a (111) plane. Its location is indicated in Fig. 2 by solid arrows. It is noted that the lattice fringes, except for the ones that are horizontal, are discontinued at the twin boundary. This is the spinel twin common in the specimens.

Small grey objects attached on the edges of the particle can be recognized as the same Rh clusters seen on the particles in Fig. 1. The clusters are revealed clearly on the periphery of the particle, whereas they are not seen in the region showing the lattice fringes for the reason already mentioned before. A facet of the (111) surface enclosed by the rectangle in Fig. 2 is enlarged and shown in Fig. 3. The clinographic view of this surface is schematically illustrated in Fig. 4. The thick arrow indicates the direction of the observation which is conducted along $[1\bar{1}0]$.

Two sizes of clusters, 6 and 10 Å in diameter, labeled "a" and "b" in Fig. 3, can be recognized. The former is close to the ideal size of six atom clusters in the $Rh_6(CO)_{16}$ carbonyl cluster. The latter ("b") may contain more than six atoms of Rh. All the clusters appear to be hemispherical. It can be concluded that the Rh_6 clusters do not have

FIG. 3. An enlarged electron micrograph corresponding to a portion of the alumina particle enclosed by a rectangle in Fig. 2. Two sizes of the Rh clusters labeled by "a" and "b" are clearly imaged on the (111) surface. Some of the clusters (marked by "c") are attached to the steps on the surface.

the so-called raft structure when they are impregnated on the (111) surfaces. It is of interest to know how these clusters are anchored to the surface of the oxygen atoms of the Al_2O_3, but it is too early to specify the details of the clusters and oxide supports.

The photograph demonstrates also that the surface steps consist of two types of atomically flat surfaces of the (111) and (001) planes (see the Miller indices in Fig. 2). The (001) surfaces appearing on the right slope of the particle do not develop as surfaces larger than those of the (111). Some of the clusters are located at the steps (labeled "c" in Fig. 3) but there is no evidence for the particles being attached preferentially on the steps. The dark lines defining the (111) surfaces consists of a row of many fine spots. The adjacent spots are separated by 2.4 Å which accords with the distance of the two adjacent Al atoms in the [1$\bar{1}$0] projection of the spinel structure.

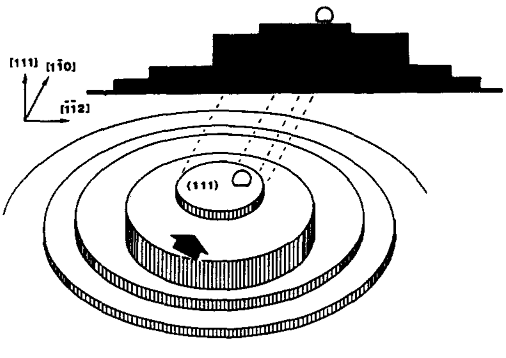

FIG. 4. Clinographic view of the surface of the alumina particle shown in Fig. 3 explaining the direction of the observation along [1$\bar{1}$0] and also the (111) surfaces.

The height of the top terrace is measured to be about 8.3 Å, which is smaller than the $d_{222} = 9.2$ Å for the ideal value for the spinel structure. The anomalously dark contrast of the top layer of the surface is caused by an electron optical artefact in the high-resolution imaging. Although the electron micrographs were recorded with great care under the condition of "optimum focus," the image details could have been affected by other factors such as the electron-beam tilt and the objective lens astigmatism (*10*). Extraction of true information on the surface atomic structure, therefore, must be made carefully.

There was evidence that some of these clusters grew larger during observation in the electron microscope, in which the clusters were irradiated by the electrons of 120 kV. Crystal growth of the Al_2O_3 particles themselves has also been observed on the surfaces. The latter observation indicates that both aluminum ions and oxygen ions can move around and be recrystallized on the particle surfaces after prolonged exposure of the specimen to the electron beam. The electron micrograph of Fig. 3 was taken carefully without excess exposure to the beam but the larger clusters indicated as "b" in Fig. 3 might have been formed by coalescence during the observation.

The study may be summarized as follows. A new type of spinel alumina has been introduced in studying catalysts of metal clusters supported on the oxides. These crystallographically and morphologically well-defined particles have made it possible to image individual small metal clusters such as Rh_6 clusters impregnated on the alumina. A good application of high-resolution electron microscopy for imaging individual metal clusters on the aluminum oxides was proposed and utilized for finding the size, shape, and adsorption sites of the clusters on the alumina supports at atomic level resolution. The Rh_6 clusters impregnated on the alumina support do not seem to have the raft structure but are hemispherical shapes following treatment of impregnated $Rh_6(CO)_{16}$ by heating at 150°C *in vacuo*.

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