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Spherical Particles and Their Surface Properties. III. Formation of Spherical Particles of Metal Oxides by O_2–H_2 Flame Fusion

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The formation mechanism of spherical particles of various metal oxides through O_2–H_2 flame fusion was investigated. Molten droplets of Al_2O_3 are solidified to form spherical particles having the structure of δ- and θ-Al_2O_3 in the surface layer and α-Al_2O_3 inside. Heat treatment of the spherical particles of Al_2O_3 at temperatures higher than 1573 K gave rise to the transition from δ- and θ-Al_2O_3 to α-Al_2O_3 and made the crystal growth, but no change in the smooth surface structure was observed, contrary to the case of TiO_2 where facetting of the surface occurred on heating. In the cases of NiO and Cr_2O_3, particles bigger than 2—3 μm in diameter are spherical, but smaller ones are apt to form single crystals. With ZnO, SnO_2, and MgO, no spherical particles were formed. It is suggested that amorphous or polymorphous substances easily form spherical particles but monomorphous ones do not. Substances, which can sublime or have higher melting point, do not give pherical particles but only single crystals.

Spherical particles having homogeneous size and smooth surface are important for research on surface and colloidal chemical properties of materials. Recent developments in the preparation of spherical latex particles promoted progress in researches in this field.[1,2] The present authors are interested in the interaction of water molecules with the surface of metal oxides, using samples with a homogeneous surface.[3–6] Recently, we have investigated the surface properties of spherical metal oxides produced by melting the particles in the O_2–H_2 flame,[7,8] as such surfaces may be expected to be homogeneous. It has been found that SiO_2 particles[7] produced by this method have excellent sphericity with smooth surfaces and a dense internal phase. Water adsorption experiments on the SiO_2 particles manifested an improvement of surface homogeneity compared to that of raw Aerosil SiO_2. In the case of TiO_2[8] it has been found that the outer layer of the spherical particles has an anatase structure and the inner part a rutile one; in contrast to SiO_2 there are many cavities inside the particles. Heat treatment of TiO_2 spheres at temperatures higher than 1073 K not only changes the anatase structure in the surface layer into a rutile one, but also promotes facetting of the spherical particle surface and finally splitting of the particles into a few rutile single crystals.

The present paper will deal with high temperature treatment of such metal oxides as SiO_2, TiO_2, SnO_2, Al_2O_3, Cr_2O_3, MgO, NiO, and ZnO in the O_2–H_2 flame and with the formation mechanism of spherical particles.

Experimental

Materials. Two kinds of raw alumina, Al_2O_3-I and Al_2O_3-II were used for the preparation of spherical particles. Al_2O_3-I is the sample pulverized from an α-Al_2O_3 ingot to give a mean particle size of 7 μm. Al_2O_3-II is aluminium oxide-C produced by Degussa; its particles are ultrafine with a particle diameter of about 20 nm; it gives broad X-ray diffraction peaks characteristic of γ-Al_2O_3. MgO powder was produced by Tokyo Electro-Chemical Industry. Both NiO and ZnO were formed by heating each metal oxalate at 873 K in air. Cr_2O_3 was formed by pyrolizing $(NH_4)_2Cr_2O_7$ at 573 K in an N_2 stream. The SnO_2 used was a commercial sample provided by Wako Pure Chemicals. These metal oxide samples were confirmed to contain only one type of crystal structure by X-ray diffraction. In the present work these materials were used without any additional treatment.

Apparatus for Preparing Spherical Particles. The facilities used for the O_2–H_2 flame treatment of metal oxides were the same as those used previously.[7] Metal oxide particles were introduced into the O_2–H_2 flame through the O_2 stream, the flame being generated by burning the mixture of 13 $L\cdot min^{-1}$ O_2 and 20 $L\cdot min^{-1}$ H_2 gases. The temperature of the flame in the furnace was determined to be higher than 2300 K over a 10 cm length from a point 7 cm below the gas nozzle by use of an optical pyrometer together with a siliconit rod. Fused particles were drawn and cooled by pumping through a 3 m duct, which is constructed from duct-1, duct-2, duct-3 of 1 m each (D_1, D_2, and D_3), stainless steel net of 100 mesh (N) and cotten gauze (G). The particles produced were collected at several positions along the flight path.

Examination of Particles. Particles treated in the O_2–H_2 flame were examined by electron microscopic observation by use of a scanning electron microscope JEOL-JSM 35, Au–Pd alloy being deposited in advance on all the samples to avoid the electrification during bonbardment by the electron beam. The particles size distribution histogram was determined by investigating more than 500 particles in electron micrographs. The crystal structure of both the raw and the product particles was established by a powder X-ray diffraction method using Cu $K\alpha$ radiation as well as with a polarizing microscope.

Results and Discussion

Formation of Spherical Al_2O_3 Particles. Figure 1 shows electron micrographs of spherical particles of Al_2O_3-I and Al_2O_3-II. The size of spherical Al_2O_3-I particles captured at any collection point is closely similar to that (6—9 μm) of non-spherical particles of the raw material; this indicates that each raw particle has been sphered individually, *i.e.*, no coalescence has occurred between them. It was also found that no cavity was present in a spherical partcle. On the contrary, spherical particles of Al_2O_3-II were very much larger than raw material particles, *i.e.*, larger than 1 μm (Fig. 1b), indicating the wide particle size distribu-

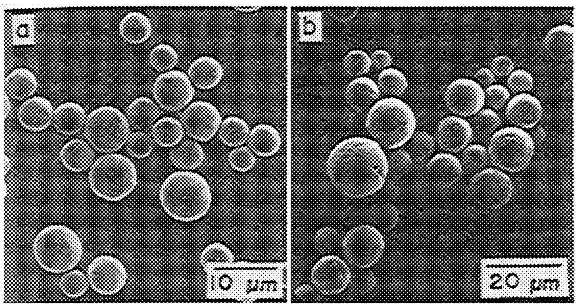

Fig. 1. Scanning electron micrographs for spherical particles of Al_2O_3-I (a) and Al_2O_3-II (b) captured at duct.

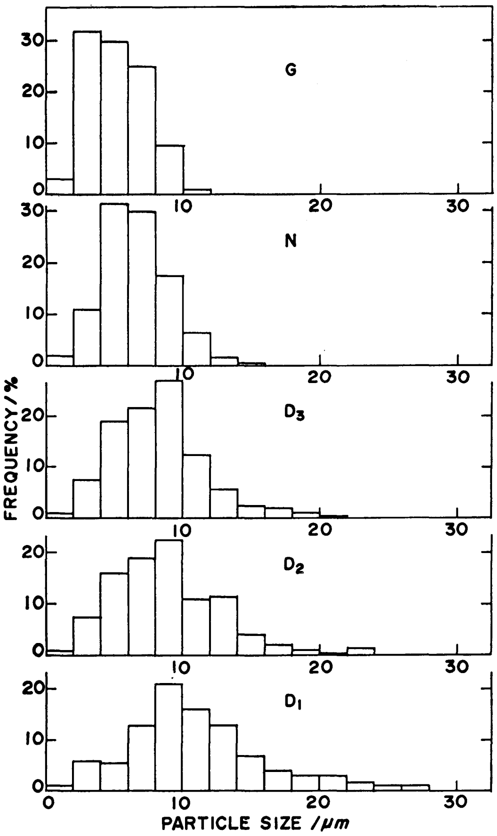

Fig. 2. Dependence of size distribution of Al_2O_3-II spherical particles on the flight distance from the furnace.

tion (Fig. 2). It is also found that the further the collection point, the smaller the mean particle size. Though the Al_2O_3-II particles look perfectly spherical, the inside of the particle is not perfectly fused and has much empty space.

The crystal structure of so formed spherical particles of Al_2O_3-I was examined by X-ray diffraction analysis. Spherical particles formed by passing through O_2–H_2 flame consist of δ- and θ-Al_2O_3, which are stable at lower temperatures, together with small portion of α-Al_2O_3, though the raw material is α-Al_2O_3 (Fig. 3). In the case Al_2O_3-II, these three structures are also observed, but their ratio varies with the collection point of the sample in the duct, α-Al_2O_3 content being much more than δ- and θ-Al_2O_3 when the particles are collected at duct-1, and less when collected at points far from the furnace, where the ratio of δ-Al_2O_3 to θ-Al_2O_3 was constant throughout the collection points. A similar situation holds also for the sample of TiO_2,[8] where the concentration of rutile exceeds that of anatase in the larger particles. These results can be interpreted as follows. Smaller particles having smaller heat capacity can be quenched so rapidly that crystal forms of δ- and θ-Al_2O_3 appeared in a large amount in the surface layer, while that of α-Al_2O_3 appeared in inner part of particles. On the bigger particles with larger heat capacity the inner part of the spherical particle is rich in α-Al_2O_3.

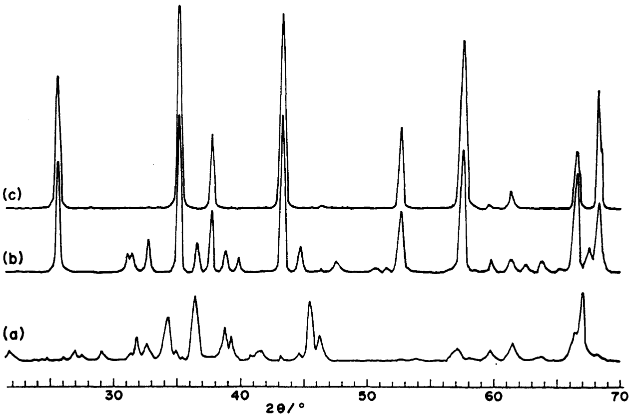

Fig. 3. X-Ray diffraction spectra of spherical Al_2O_3-II particles determined by using the radiation of Cu $K\alpha$.
a: As-grown sample including the crystal structures of α-, δ-, and θ-Al_2O_3, b: 1473 K-treated, α- and θ-Al_2O_3, c: 1573 K-treated, α-Al_2O_3.

When the spherical particles of Al_2O_3 are heated for 4 h up to 1373 K, the X-ray diffraction spectrum remains almost unchanged. Upon calcination at 1473 K δ-Al_2O_3 disappeared, θ- and α-Al_2O_3 being left (Fig. 3b). Treatment of the sample at temperatures higher than K led to the complete transition of crystal structure from θ-Al_2O_3 to α-Al_2O_3 (Fig. 3c). Contrary to the TiO_2 particles, however, no facetting of the particle surface was observed upon heat treatment, even at higher temperatures, in spite of the drastic changes in crystal structure. What appeared here was merely a smoothing of the particle surface and charging up of the particle during SEM observation. This might have stemmed from the increased insulation upon dehydration by heat treatment. Polarizing microscope observation of so grown spherical Al_2O_3 particles under crossed nicols showed small spots in a vague back ground, probably because of the polycrystallinity of the particles. After the crystal structures were changed into α-Al_2O_3 by heat treatment, the small spots decreased in number and became brilliant, which indicates that the heated spherical particle has mosaic structure of a few well grown α-Al_2O_3 crystallites, as reported by Nelson *et al.*[9] on Al_2O_3 spheres.

Formation of Spherical Particles of Metal Oxides by Means of O_2–H_2 Flame Treatment. Like SiO_2 and TiO_2 particles, it has been ascertained that spherical particles of Al_2O_3 can be produced through O_2–H_2 flame fusion

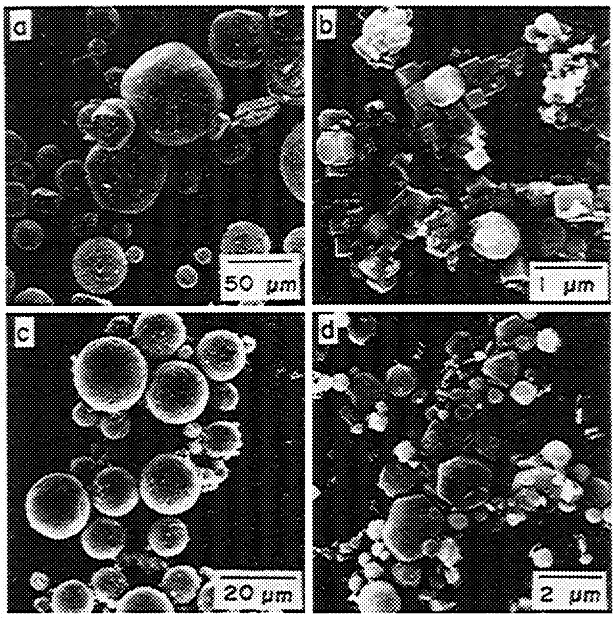

Fig. 4. Scanning electron micrographs for NiO and Cr_2O_3 particles treated through O_2–H_2 flame.
a: NiO at D_1, b: NiO at G, c: Cr_2O_3 at D_1, d: Cr_2O_3 at G.

irrespective of the preparation method of raw materials. However, there are some metal oxide samples that it is difficult or impossible to make spherical. Figure 4 demonstrates electron micrographs for NiO and Cr_2O_3 particles treated in the O_2–H_2 flame. Larger particles of both metal oxides are almost spherical have wrinkles in the surface, but those of NiO having a smooth surface are cubic. With larger particles of NiO, a small amount of contamination by Ni metal was detected by X-ray diffration; this indicates partial dissociation of NiO at higher temperatures. Smaller NiO particles collected on gauze have a characteristic cubic shape; some of them are lacking corners. In the case of Cr_2O_3 particles the shape changed from sphere, through short hexagonal rod, to hexagonal platelet as the size decreased. Inner structure of spheres of metal oxides is similar to that of Al_2O_3 and includes many cavities. It is interesting here that despite the presence of cavities, the NiO particles obtained near the furnace are apt to become cubic. By considering this fact together with the result that apparently spherical having cavities approach the cubic particle by heating at 1473 K (Fig. 5a), it can be understood that a molten NiO particle is apt to take up an ordered arrangement of atoms and to form almost a single crystal sphere. On the other hand, change in the surface structure of Cr_2O_3 spheres upon calcination is very similar to that of TiO_2:[8] heat treatment results in facetting to split a particle into single crystals (Fig. 5b).

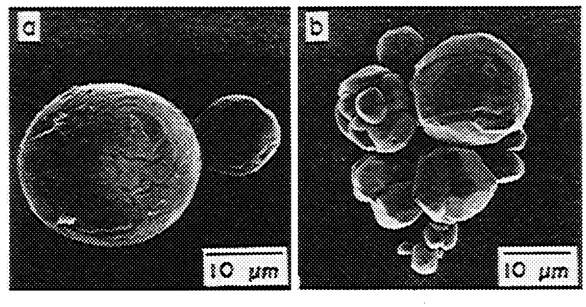

Fig. 5. Scanning electron micrographs for spherical particles of NiO (a) Cr_2O_3 (b) heated at 1573 K for 4 h.

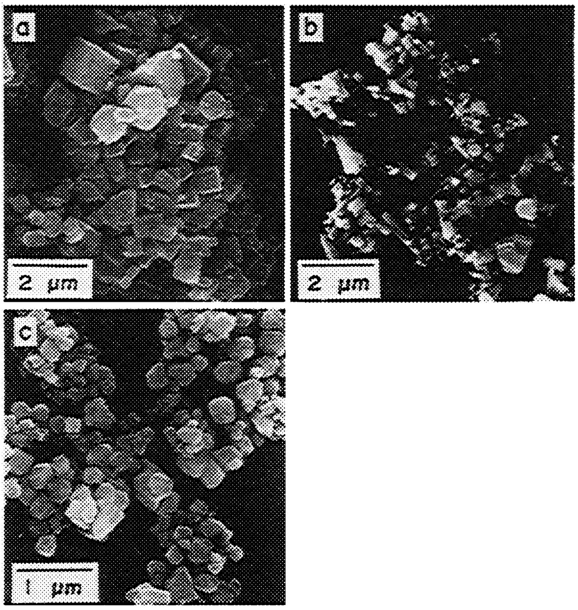

Fig. 6. Scanning electron micrographs for MgO (a), ZnO (b), and SnO_2 (c) particles treated through O_2–H_2 flame and captured at gauze.

When metal oxides such as MgO, ZnO, and SnO_2 were passed through the O_2–H_2 flame, the particles obtained were not spherical but polyhedral, having well defined crystal planes. As shown in Fig. 6, smaller particles collected by gauze are single crystals of each crystal structure of the metal oxides: cubes for MgO, needlelike single crystals with well defined prism planes $(10\bar{1}0)$ for ZnO, similar to those produced by burning Zn metal in air,[4] and polyhedra for SnO_2 in which some particles are octahedral, that is trigonal planes are exposed. Similar particles have been formed by oxidizing SnO vapour at 1423 K in air,[10] where the trigonal face was identified to be the (111) plane by electron diffraction.

As has been discussed above, the possibility whether metal oxide particles formed by the O_2–H_2 flame fusion are spherical or not seems to depend upon the nature of metal oxide. Next, let us consider the reason for this phenomenon on the basis of data shown in Table 1. Using our technique for producing spherical particles, to produce a decrease in the surface free energy of a molten metal oxide particle on sphering, it is necessary that the temperature of the O_2–H_2 flame is higher than the melting point of the sample. With SiO_2, TiO_2, and Al_2O_3, as can be expected from data in Table 1, this condition is found to be satisfied, since spherical particles were obtained.

It would be anticipated that smaller particles would be more easily liquified to give spherical particles than larger ones. With TiO_2 and Al_2O_3, this expectation is

Table 1. Physical properties and sphericity of metal oxides

Metal oxide	$\frac{\mathrm{Mp}}{\mathrm{K}}$	Crystal structure	Sphericity
Al_2O_3	2320	α-, δ-, θ-Al_2O_3	Yes
TiO_2	2143	Rutile, Anatase	Yes
SiO_2	1883 (quartz)	Amorphous	Yes
NiO	2230	NaCl	Difficult (spheres, single crystallites)
Cr_2O_3	2607 2530 (sublimate)	α-Al_2O_3	Difficult (spheres, single crystallites)
ZnO	2073 (sublimate)	Wurtzite	No (single crystallites)
SnO_2	1898 (sublimate)	Rutile	No (single crystallites)
MgO	3073	NaCl	No (single crystallites)

valid, but with NiO and Cr_2O_3, the inverse is truth. The larger particles are spheres and the smaller ones fine single crystals, though the flame temperature exceeds the melting point. The data in Table 1 lead to a conclusion that one simple rule is involved in the present phenomena. Namely, such metal oxides as SiO_2, TiO_2, and Al_2O_3 which easily form spheres have amorphous or polymorphous structures, while NiO and Cr_2O_3, which have lower ability to produce spheres, are crystallized monomorphously. This interrelationship can be interpreted as follows. First, NiO forms cubic particles not only of the smaller ones but also for the larger ones sedimented in duct 1. Cr_2O_3 particles with fairly large size (4—7 μm) are hexagonal prisms (almost spheres) with about the same length of the diagonal distance and height. That is, these two molten oxides have a strong tendency to form single crystal particles. It is well known that the liquid, at temperatures not much higher than the melting point, is composed of a number of small domains which retain the ordered structures of the solid even below the melting point. In the case of small molten particles of monomorphous metal oxides, it may be considered that the liquid domains of the same quasi-crystal structure unite to control the shape of the particle. Barry *et al.*[11] obtained fine spherical particles of Cr_2O_3 (<0.1 μm) besides hexagonal platelets from CrO_2Cl_2 by the induction plasma torch method. The ease of formation of fine spheres in their experiments seems to differ from that reported here, but this may be explained as follows. They raised the temperature of the furnace to 5000 K which is much higher than that in the present case; the spherical liquid droplets formed would have lost any ordered structure and would be quenched as spherical particles.

Secondly, the molten particles of Al_2O_3 or TiO_2, which are polymorphous, will possibly have a number of domains with different crystal structures just like polycrystalline particles from time to time and from place to place, in contrast to the case of monomorphous oxides. Such a molten particles should be isotropic to form spherical particles due to surface tension. It will easily be understood that the spherical glassy SiO_2 droplet has been solidified as it stands in a liquid state.

ZnO and SnO_2, have sublimation temperatures lower than the flame temperature and therefore no liquid phase is present under our conditions. Thus, it will be reasonable to conclude that particles of these two oxides sublimed to recrystallize as fine single crystallites at relatively lower temperatures. For MgO, the melting point is much higher than the flame temperature; accordingly spherical particles were not formed but the crystal growth of well defined cubic particles proceeded during the O_2–H_2 flame treatment.

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