

Abstract

Ceria-zirconia solid solution is essential as a catalytic promoter in three-way catalysts used to clean automobile exhaust gas in order to meet recent severe emission controls. There are many synthesis methods reported in recent years for the synthesis of ceria-zirconia solid solution. However, few reports exist concerning synthesis methods that use mechanical energy of hard milling. The only previous report is by the present authors' and concerns a wet milling process for synthesizing solid solution that is expected to provide a material with high specific surface area. The formation mechanism must be elucidated, because few previous reports exist concerning the phenomena of forming solid solution between whole oxides at around room

temperature by the wet milling process. It is necessary to clarify the formation mechanism in order to apply this process to make solid solutions between oxides other than the ceria-zirconia system. The formation mechanism of ceriazirconia solid solution was examined through the analysis of the phenomena of the formation of the solid solutions by the wet milling process. The mechanism was so-called "mechanical alloying", a phenomenon in which materials are mixed at the atomic level by mechanical energy. The crystallite size of the ceria-zirconia solid solution by the wet milling process finally reached 20 nm, which is thought to be the "critical particle size" at which the fracture mode changes from brittle to ductile.

Keywords

Automobile catalyst, Exhaust gas, Ceria, CeO₂, Zirconia, ZrO₂, Solid solution, Oxygen storage capacity, Wet milling, Mechanical alloying

1. Introduction

A three-way catalyst containing noble metals, mainly platinum rhodium and palladium, and catalytic promoters is used to purify exhaust gas from an automobile. The activity of the catalyst reaches a maximum, when the exhaust gas is nearly neutral, or at stoichiometric composition to oxidize components such as NO and molecular oxygen and to reduce components such as HC, H₂ and CO. The oxygen storage capacity of the catalytic promoter is effective for maintaining the neutral atmosphere in the exhaust gas. In recent years, ceria-zirconia solid solution has become an indispensable material for use as a catalytic promoter in three-way catalysts to purify automotive exhaust at high levels because ceria-zirconia solid solution has a large oxygen storage capacity.⁷⁾

Trovarelli et al. reported that ceria-zirconia solid solution having a specific surface area of approximately 20 m²/g could be fabricated by highenergy mechanical milling in dry conditions.⁴⁾ Small particles in the sub-micrometer region generally cannot be fabricated easily by milling under dry conditions because the cohesion of each particle becomes so strong that the particles cannot be broken down effectively into smaller sized particles in the region. Milling under wet conditions is thought to be more suitable for fabricating smaller particles having a larger specific surface area than that under dry conditions.

The formation of ceria-zirconia solid solution at around room temperature by the wet-milling process was previously reported by the present authors.^{5, 6)} Ceria and zirconia uniformly dissolved each other in the solid solution. The formation mechanism of uniform solid solution between ceria and zirconia must be elucidated, because few previous reports exist on phenomena of solid solution formation between whole oxides at around room temperature by the wet milling process. It is necessary to clarify the formation mechanism in order to apply this process to make solid solutions between oxides other than the ceria-zirconia system. The formation mechanism of ceria-zirconia

solid solution by solid phase reaction via wet milling is reviewed herein.

2. Experimental

An attrition mill was used for sample preparation. The milling apparatus used was an attrition mill, as shown in Fig. 1, which is used in every experiment to prepare solid solution samples by the milling method.⁵⁻⁸⁾ The milling media of the mill consists of balls, a vessel and agitator disks made of zirconia containing 3 mol% Y₂O₃ (yttria partially stabilized zirconia). The agitator disks were rotated at 2000 to 4200 rpm. The acceleration applied to the balls charged in the vessel of the mill becomes approximately 1000 times larger than gravity at 4200 rpm. Two types of ceria powders were used as a starting material: one having an average agglomerated grain-size of 10 μ m, a purity of 99.9%, and a specific surface area of 120 m^2/g (referred to as high-SSA CeO₂), and the other having a specific surface area of 4 m^2/g , an average agglomerated grain size of 3 μ m, and a purity of 99.9% (referred to as low-SSA CeO₂). Zirconia powder having an average agglomerated grain-size of 1.1 μ m, a purity of 99.5% and a specific surface area of 100 m²/g was used as a starting material for an experiment using high-SSA CeO₂. Sialon (Si_3N_4) solid solution) powder, a much harder material than zirconia, as well as ceria, having an average agglomerated grain size of 5 μ m and a specific surface area of $1 \text{ m}^2/\text{g}$ was added in order to



Fig. 1 Schematic illustration of attrition mill (Willy A. Bachofen AG DYNO MILL KDL type).

examine the formation of ceria-zirconia solid solution in the absence of contact stress between the ceria and zirconia powders. In the process, the larger grains of Sialon present between the balls and the mill surface prevents the powders from being stressed by the balls. The concentration of Si, Al, Y, O and N in the Sialon powder is 44.2, 9.9, 7.9, 4.9 and 35.0 mol% respectively.

Ethanol having a purity of 99.5% or ionexchanged water were used as the dispersant. A slurry containing 100 g of ceria powder was milled in order to study the change in grain size or specific surface area upon milling. As milling proceeded, zirconia powder was produced by the balls, vessel and agitator disks as a result of the abrasion between them. The supplied zirconia (containing 3 mol% Y_2O_3) acted as a chemical agent to form the solid solution. The specimen, milled for a certain number of hours, was examined via the X-ray diffraction method using $CuK\alpha$ or $CoK\alpha$ radiation. The specific surface area of the powders was measured using the single point BET (after Brunauer, Emmett and Teller) method, and the particle size was estimated from the surface area. The crystallite size was estimated based on the half-width of the X-ray diffracted from the specimen using Scherrer's formula.⁹⁾ The amount of worn zirconia powder mixed from the milling media into the ceria powder was estimated based on the weight loss of the milling media. The data of the solid solution powder made from low-SSA CeO_2 are examined by comparison with those of the solid solution powder made from high-SSA CeO_2 .

3. Results and Discussion

Total weight loss of the milling media was 65.2 g after 44 hours of milling for low-SSA CeO_2 .⁸⁾ This weight loss corresponds to the amount of worn zirconia powder mixed into the slurry of the ceria powder. The amount is almost the same as that for the milling of high-SSA CeO_2 .⁶⁾ Therefore, the wear rate of the media during milling for the low and high-SSA CeO_2 is almost the same.

X-ray diffraction patterns of the high-SSA CeO₂ are shown in **Fig. 2**, which is referenced from a previous paper.⁵⁾ The X-ray diffraction line of the high-SSA CeO₂ remained at the same position from 0 to 4 h. The (311) peak remained at 56.3° until 4 h, and then began to shift to a higher angle and reached 59.1° after 45 h of milling. The gradual shift from 8 to 45 h demonstrates that the high-SSA CeO₂ reacted with the worn zirconia powder uniformly and that the composition of the ceria-zirconia solid solution was maintained uniformly as a whole. The reason for the remaining diffraction lines in the initial stage of milling is thought to be that a certain



Fig. 2 X-ray diffraction patterns of fine ceria powder before and after milling, using $CuK\alpha$. This figure is referenced from previous paper⁵⁾ and slightly modified.

amount of time is required for the 10 μ m agglomerates of high-SSA CeO₂ to break down to the critical particle size at which the worn zirconia particles can dissolve in the ceria particles.

The lattice constant of the solid solution was determined from the diffraction angle, which is shown in **Fig. 3** as a function of zirconia content supplied from the balls, vessel and agitator disks, or the weight gain. The function is linear and agrees with the line connecting the constants of pure CeO_2 and pure ZrO_2 , i.e. follows Vegard's rule.¹⁰⁾ This proves that the ceria and zirconia powder form a solid solution having a valence of 4.

Figure 4 shows the diffraction pattern of high-SSA CeO₂ powder after milling in water. The formation of CeO₂-ZrO₂ solid solution occurred in the milling by changing the dispersant from ethanol to water. **Figure 5** shows the diffraction pattern of high-SSA CeO₂ and ZrO₂ powders after milling in ethanol. CeO₂ from the high-SSA CeO₂ powder dissolved with ZrO₂ from the ZrO₂ powder as well as with ZrO₂ from the milling media. These results suggest that no reaction contribute like alcoxide formation between the liquid phase of the dispersant and the solid phases for the formation of the CeO₂-ZrO₂ solid solution. **Figure 6** shows that the





formation of the solid solution by Sialon powder is almost impossible in the milling of 100 g of high-SSA CeO₂, 50 g of ZrO₂ and 90 g of Sialon powder. If the interaction of ceria and zirconia with the liquid (ethanol) is sufficient for the formation, the solid solution should be formed in the process even in the presence of Sialon. However, little solid solution is



Fig. 4 Diffraction pattern of CeO₂ powder after milling in water, near (311), using CoK α . Stating material: CeO₂, rotational speed: 4200 rpm. This figure is referenced from previous paper.⁶⁾



Fig. 5 Diffraction pattern of CeO₂ and ZrO₂ powder after milling in ethanol, near (311), using CoK α . Stating material: CeO₂ and ZrO₂, rotational speed: 4200 rpm. This figure is referenced from previous paper.⁶⁾

formed in the process. Thus, the "solid process", or the reaction of the solid, ceria powder, with the solid, zirconia powder, should be the predominant process for the formation of solid solution. Assuming this mechanism, the results due to the addition of Sialon and zirconia powders are



Fig. 6 Diffraction pattern of CeO₂ powder after milling, near (311), using CoK α . Stating material: 100g of CeO₂, 50g of ZrO₂ and 90 g of Sialon, rotational speed: 4200 rpm. This figure is referenced from previous paper.⁶ explained as follows: The hard material, Sialon can provide some space between the balls, between the balls and the vessel, and between the balls and the agitator disks. The ceria and zirconia powders can exist in this space, and can thus be prevented from hard contact with one another, with the vessel, or with the disks, resulting in limited formation or reduced formation of the solid solution.

The diffraction pattern of the low-SSA CeO₂ reveals that the original diffraction lines from the high-purity ceria do not shift even after 44 hours of milling (Fig. 7, (311) of original CeO₂), and that new diffraction lines appear at a higher angle than the original lines and are separate from the original lines. The new lines are evident at the milling time of 36 h (Fig. 7, (311) of CeO₂-ZrO₂ solid solution). The new lines increase in intensity as the intensities of the original lines decrease with the progress of milling. The lines are all indexed to those of the solid solution of ceria and zirconia. The diffraction lines of the solid solution appear to increase without a gradual shift from the original lines. One line appears suddenly at an angle of 58.2°, indexed as diffraction line (311), and its intensity increases without any shift, indicating that little solid solution is formed before the milling time of approximately



Fig. 7 X-ray diffraction patterns of ceria powder after a given milling time, using CuK α . O shows peaks from CeO₂-ZrO₂ solid solution. Stating material: ceria powder, milling media; zirconia dispersant; ethanol, rotational speed; 4200 rpm.

27 h, and also that the solid solution is formed at the composition corresponding to the diffraction angle of 58.2° , or at the lattice constant of 0.527 nm.

Figure 8 is referenced from a previous paper.⁶⁾ The specific surface area of the low-SSA CeO₂ milled for 44 h is 45 m^2/g , as shown in Fig. 8. The area, 45 m²/g, corresponds to the average grain size of 21 nm, assuming the powder to be spherical. The half-width of the diffraction line of the original ceria powder increases gradually with the milling time and reaches approximately 0.55° for the line of (311) at 27 h, and 0.70° at 44 h. Applying Scherrer's formula to the half-width, the grain size of the original ceria was estimated as 28 nm at 27 h, and 21 nm at 44 h. The crystallite size of the original ceria powder (the low-SSA CeO_2), as estimated by Scherrer's formula, is shown in Fig. 9 as a function of milling time. The size is in good agreement with that estimated from the surface area (Fig. 8). The specific surface area of the low-SSA CeO₂ is $4 \text{ m}^2/\text{g}$, which corresponds to a diameter of 200 nm. The diameter estimated from the half-width of the X-ray diffraction peak is also 200 nm. These values are in good agreement. Thus, the crystallite size of the low-SSA CeO₂ is 200 nm. After the agglomerate of the powder disappears, the crystallite size corresponds to the particle size calculated from the specific surface area. The solid solution can be



Fig. 8 The specific surface area of low and high-SSA CeO₂ before and after milling. This figure is quoted from previous paper.⁵⁾

clearly detected at 36 h. At which point, the grain size of the low-SSA CeO₂ is approximately 22 nm on average, using any method of estimation. The decreasing rate of crystallite diameter of the original ceria powder (the low-SSA CeO₂) becomes small for milling between 36 and 44 h, as shown in Fig. 8. The crystallite size appears to asymptotically approach 20 nm. This shows that the original ceria particle smaller than 20 nm reacts with zirconia, yielding the solid solution, and that the intensity of the peak of the original ceria decreased with no further broadening beyond 0.70° after 36 h of milling, as shown in Fig. 7. The critical size, 20 nm, calculated from the half-width of the XRD peak, at which ceria and zirconia particles begin to react in the milling agrees with the diameter, 20 nm, estimated from the specific surface area (Fig. 8).

A schematic diagram of the dissolving process of the low and high-SSA CeO_2 with worn zirconia powder is shown in **Fig. 10**. For the case of high-SSA CeO_2 , its agglomeration is easily dispelled in the initial stage of milling. Almost all particles are of less than the critical size of 20 nm. As milling proceeds, zirconia particles were added due to wear of the milling media and these particles dissolved into the ceria particles. The worn zirconia powder dissolves promptly into ceria particles of less than critical size. The powder being milled changed into



Fig. 9 Crystallite diameter of original ceria powder (low-SSA CeO₂) calculated by Scherrer's formula as a function of milling time.

the ceria-zirconia solid solution as a whole. The solid solution particles finally reach the critical size of 20 nm. In contrast, the particle (crystallite) size of the low-SSA CeO₂ is larger than the critical size, and the large crystallites are difficult to simultaneously break into small pieces of less than 20 nm. These particles are partially broken down into smaller particles, and only the broken-down particles dissolved with worn zirconia particles form a solid solution of ceria and zirconia. The solid solution particles enlarge to 20 nm. The original low-SSA CeO₂ remained until 44 h.

For the milling of low-SSA CeO₂, the ceriazirconia solid solution formed exhibits a diffraction angle of 58.2° of the (311) plane in Fig. 7. The diffraction angle of 58.2° of (311) of the solid solution corresponds to the composition of 50 mol% CeO₂-50 mol% ZrO₂, as shown in a previous paper.⁶⁾ The composition occurred predominantly during the milling of the low-SSA CeO₂. The reason for the preferred occurrence of the composition was that the supply rates of broken-down ceria particles of less than critical particle size from the low-SSA CeO₂ and worn zirconia powder from the milling media may be almost the same.

As mentioned above, the specific size of each particle, which is dissolving, cannot be measured by

the X-ray diffraction method or the specific surface area measurement. However, the value of 20 nm, which is considered to be the critical particle size, was found asymptotically using these two methods, the results of which were in good agreement. Therefore, the critical particle size may be reliable. The important point to remember in fabricating a new material by this process is to use starting materials that have a smaller crystallite size than the critical particle size.

Conclusions

1) The formation of ceria-zirconia solid solution by the process of milling ceria powder using zirconia milling media in liquid was proved to be a result of a solid phase reaction between ceria and zirconia powders induced by contact stress.

2) The reaction that forms the ceria-zirconia solid solution from large ceria particles $(4 \text{ m}^2/\text{g})$ begins after 27 h of milling, which is much longer than the beginning of the reaction of the high-SSA CeO₂.

3) The critical particle size of ceria powder to begin the reaction with zirconia is thought to be approximately 20 nm, which was found asymptotically by two methods, X-ray diffraction and specific surface area measurements.

4) The reason for the preferred occurrence of the



Fig. 10 Schematic diagram of the dissolving process of the low and high-SSA CeO₂ with worn zirconia powder.

solid solution, 50 mol% CeO_2 -50 mol% ZrO_2 is considered to be that the supply rate of ceria particles smaller than the critical particle size from the low-SSA CeO_2 and worn zirconia powder from the milling media maybe almost identical, and that the two kinds of fine powders react with each other uniformly.

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