Effects of Solvent on Powder Characteristics of Zinc Oxide and Magnesia Prepared by Flame Spray Pyrolysis

Takao TANI, Akane KATO* and Hideaki MORISAKA
Inorganic Materials Lab., Toyota Central R & D Labs., Inc., Nagakute, Aichi 480-1192
*Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya-shi 466-8555

Zinc oxide (ZnO) and magnesia (MgO) powders were made by flame spray pyrolysis of zinc acetate and magnesium acetate, respectively, dissolved in methanol-water mixture. The product powders were characterized by nitrogen adsorption, infrared adsorption (IR), X-ray diffraction (XRD) and transmission electron microscopy. The effects of solvent on powder characteristics were examined by changing methanol content (X = 1 – 0.4) in the solvent. Polyhedral aggregates of nanoparticles were formed by evaporation, condensation and oxidation of the metal species in the spray flame. Decrease of the methanol content to X = 0.4 lowered the spray flame temperatures, suppressing complete evaporation of the metal species and particle formation in the gas phase. Decrease of the methanol content to X = 0.4 lowered the spray flame temperatures, suppressing complete evaporation, resulting in a mixture of nanoparticles and large (e.g. > 100 nm) particles for both ZnO and MgO syntheses. On the other hand, the XRD and IR spectra indicated partial hydroxide formation for MgO synthesis, differed from ZnO synthesis. The reaction with water vapor in the combustion gas can be enhanced for MgO because of the larger Gibbs energy change for hydroxylation in MgO than in ZnO.

Key-words: Zinc oxide, Magnesia, Nanoparticles, Flame spray pyrolysis, Gas phase reaction

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1. Introduction
Flame spray pyrolysis (FSP) is an elegant process to make metal oxide nanoparticles by spraying and combusting precursor solutions in which metal salts are dissolved in organic solvents. Product particles are formed in the gas phase by evaporation, condensation and oxidation of the metal species (e.g. atoms or oxide clusters). A broad spectrum of precursors can be used for powder synthesis, which is an advantage for FSP compared with conventional flame aerosol synthesis where gas-phase precursors are used.

Selection of the precursor is very important for FSP because evaporation of the metal species in the spray flame is required for nanoparticle formation. In case of alumina particles synthesis, complete evaporation took place when using aluminum alkoxide as precursor, forming nanoparticles, whereas FSP of aluminum nitrate resulted in large (e.g. > 100 nm) spherical particles by drying of the dispersed droplets followed by oxidation of the precursor without evaporation of the metal species as seen with spray pyrolysis. Also for silica synthesis, nanoparticles and large spherical particles were obtained from hexamethyldisiloxane and silica sol, respectively. On the other hand, solvent used for synthesis can influence product particle morphology. Mäder et al. reported that large (e.g. > 100 nm) particles in addition to nanoparticles were formed for ceria synthesis by FSP from the cerium acetate/acetiacid precursor solution, whereas addition of an isooctane/2-butanol mixture to the solvent increased the combustion enthalpy of the solvent, achieving complete evaporation, forming only nanoparticles.

Here, zinc oxide (ZnO) and magnesia (MgO) particles were made by FSP of zinc and magnesium acetate, respectively, using solvents with various methanol/water ratios. Boiling points of these oxides (ZnO: 1975°C [Sublimation point], MgO: 3600°C) are quite different, which may influence evaporation behavior of the metal species in the spray flame. Therefore, it is of interest to better understand how the solvent affects product particle characteristics of these oxides.

2. Experimental
Zinc acetate dihydrate (ZA: Wako, S grade) and magnesium acetate tetrahydrate (MA: Wako, S grade) were used as Zn and Mg source, respectively. The precursors were dissolved in mixtures of methanol (Wako, S grade) and deionized water with volume ratios of methanol/water = 100/0, 80/20, 60/40 and 40/60, resulting in 0.5 mol/L precursor solutions.

Powder synthesis was carried out using a spray flame reactor. The detailed configurations of the reactor were shown elsewhere. A pump supplied the precursor solution at a feed rate of 12 cm³/min to the nozzle where the solution was dispersed into droplets by oxygen of 11 L/min. The droplets were ignited by supporting methane/oxygen flames surrounding the nozzle. The total flow rates of methane and oxygen were 2 L/min each. Excess oxygen of 15 L/min was supplied through a porous metal plate ring. At this combustion condition, the adiabatic temperatures of the flames were 3240, 2740, 2230 and 1710°C for the solvents with methanol/water ratios of 100/0, 80/20, 60/40 and 40/60, respectively, without precursors.

The product particles were collected on a Gore–Tex filter sheet with the aid of a vacuum pump. Powder synthesis was carried out twice for all experiments.

The particle morphology was observed by transmission electron microscopy (TEM: Nikon DenShi, JEM2000EX, 200 kV). The crystalline phase was identified by X-ray diffraction (XRD: Rigaku, RINT1500V, 40 kV, 300 mA) at 2θ (Cu Kα) = 20–70° and scan speed = 2°/min. The crystallite size (d_{XRD}) was calculated using Scherrer’s equation from the full width at half maximum.
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Fig. 1. X-ray diffraction patterns of the FSP-made ZnO powders from various precursor solutions with methanol/water ratios of 100/0 (Z100), 80/20 (Z80), 60/40 (Z60) and 40/60 (Z40).

Fig. 2. X-ray diffraction patterns of the FSP-made MgO powders from various precursor solutions with methanol/water ratios of 100/0 (M100), 80/20 (M80), 60/40 (M60) and 40/60 (M40).

at half maximum of the strongest diffraction peak. The specific surface area (SSA) was measured by nitrogen adsorption (Micro Data, 4232). The BET-equivalent average primary particle diameter \( d_{\text{BET}} \) was obtained from the measured SSA and solid density (ZnO: 5.6 Mg/m\(^3\), MgO: 3.6 Mg/m\(^3\))\(^{30} \) by \( d_{\text{BET}} = 6 / (\text{SSA} \cdot \rho) \), assuming solid spherical particles. The remained acetates were detected by infrared (IR) spectroscopy (Nicolet, Avantar 360).

All powders were labeled by composition (ZnO: Z, MgO: M) and methanol/water ratio (100/0: 100, 80/20: 80, 60/40: 60, 40/60: 40), so ZnO made using the solvent with methanol/water = 100/0 is labeled as Z100.

3. Results

Figures 1 and 2 show XRD patterns of the FSP-made ZnO and MgO powders, respectively. The peaks from zincite (ZnO: #36–1451) were identified and other phases (e.g. acetates and hydroxides) were not detected for all ZnO powders. On the other hand, secondary phases in addition to periclase (MgO: #45–0946) were observed for all MgO powders. A very broad peak typical for amorphous phase at 25–35° existed for M100 and M80. The peaks from magnesium hydroxide (444–1482), acetate hydrate (14–0282) and unknown phase were seen for M60. Acetate hydrate and the unknown phase were detected also for M40.

Figure 3 shows IR spectra (a: 2500–3500 cm\(^{-1}\), b: 1000–2000 cm\(^{-1}\)) for the precursors (ZA and MA) and product powders. The absorption peaks were accentuated by a factor of four in Fig. 3(a) because they were weaker than those in Fig. 3(b). Absorption peaks (Fig. 3(b)) from ZA and MA existed for Z40 and M40, respectively, suggesting the precursor was not decomposed completely. Very weak absorption peaks from ZA and MA were noticed also for Z60 and M60, respectively. Almost no absorption typical for ZnO\(^{33} \) was observed for Z80 and Z100. A peak at \( \sim 1430 \) cm\(^{-1}\) from Mg–O bonding\(^{33} \) was seen for M100 and M80. On the other hand, a broad peak at \( \sim 3300 \) cm\(^{-1}\) (Fig. 3(a)) possibly attributed to O–H bonding (e.g. hydroxides and/or adsorbed water)\(^{33} \) was detected for Z40 and all MgO powders.

Table 1 summarizes SSA, \( d_{\text{BET}} \) and \( d_{\text{XRD}} \) of the product powders. The \( d_{\text{BET}} \) were 28, 24, 27 and 86 nm and the \( d_{\text{XRD}} \) were 24, 20, 21 and 9 nm for Z100, Z80, Z60 and Z40, respectively. The \( d_{\text{BET}} \) and \( d_{\text{XRD}} \) were roughly consistent with each other and they were not changed so much by the solvent for Z100, Z80 and Z60. The \( d_{\text{BET}} \) and \( d_{\text{XRD}} \) were far larger and smaller, respectively, for Z40 than those for Z60. On the other hand, the \( d_{\text{BET}} \) were 27, 28 and 16 nm for M100, M80 and M60. The \( d_{\text{BET}} \) was similar for M100 and M80 but decreased for M60. Here, the result for M40 was neglected because SSA of M40 was not reproducible (varied from 19 to 87 m\(^2\)/g). The degassing temperature (200°C) for SSA measurement was higher than the decomposition temperature of MA (80°C)\(^{30} \) and therefore the remained MA (Fig. 3) would be decomposed during degassing, which may have resulted in the varying of the SSA. In contrast, the higher decomposition temperature of ZA (237°C)\(^{30} \) than the degassing one can
reproduce the SSA for Z40 in spite that the precursor was remained. The \(d_{\text{XRD}}\) were not changed by the solvent and were 11, 11, 9 and 11 nm for M100, M80, M60 and M40, respectively. The \(d_{\text{BET}}\) and \(d_{\text{XRD}}\) were not consistent with each other for all MgO powders. These results were different from those for the ZnO powders.

Figure 4 shows TEM images for Z100, Z40, M100 and M40. Polycrystalline aggregates of nanoparticles, typically seen in flame-made powders, were observed for Z100 and M100. The average primary particle diameters \(d_{\text{TEM}}\) obtained by counting 30 particles were about 30 and 50 nm for Z100 and M100. The \(d_{\text{TEM}}\) was in agreement with \(d_{\text{BET}}\) \((28 \text{ nm})\) for Z100, whereas the \(d_{\text{TEM}}\) was far larger than \(d_{\text{BET}}\) \((27 \text{ nm})\) for M100. On the other hand, large \((e.g., > 100 \text{ nm})\) particles in addition to nanoparticles were seen frequently for Z40 and M40, and the fractions of the large particles were similar to each other for both powders. Such large particles were not found for Z80, Z60, M80 and M60.

4. Discussion

The particle morphology suggested complete evaporation of the metal species in the spray flame and particle formation in the gas phase for Z100, Z80, Z60, M100, M80 and M60. On the other hand, the low flame temperature can suppress the evaporation, leading to particle formation both in the gas and liquid phases, resulting in a mixture of nanoparticles and large particles. In addition, the low flame temperature can also suppress decomposition of the precursor for Z40 and M40, showing the obvious absorption peaks from the acetates in the IR spectra. The criteria for complete evaporation was not changed for both ZnO and MgO synthesis by FSP in these experimental conditions in spite that the boiling points of these oxides as well as the decomposition temperatures of their precursors were quite different. Further experiments are necessary to understand what property dominates the evaporation behavior of the metal species by FSP.

The absorption from O–H bonding was not observed in the IR spectra for Z100, Z80 and Z60, whereas it was seen for M100, M80 and M60 in spite of almost complete decomposition of the precursor. The Gibbs energy changes for hydroxylation are \(-4.4\) and \(-35.6 \text{ kJ/mol}\) for ZnO (ZnO + H\(_2\)O(gas) → Zn(\(\text{OH}^+\))\(_2\)) and MgO (MgO + H\(_2\)O(gas) → Mg(\(\text{OH}^+\))\(_2\)), respectively, indicating MgO is more likely to form its hydroxide than ZnO. The MgO aerosol can be reacted with water vapor, generated by combustion of methane and the precursor solution and contained in the solvent, in the cooling zone and/or on the filter, forming hydroxides. The very broad peak at 25–35° in the XRD spectra may correspond to amorphous magnesium hydroxide for M100 and M80. In addition, a high amount of the water vapor in the combustion gas may enhance hydroxylation, resulting in the peaks from magnesium hydroxide in the XRD spectra and the increase of the SSA for M60.

For Z100, Z80 and Z60, the agreement of the \(d_{\text{BET}}, d_{\text{XRD}}\) and \(d_{\text{TEM}}\) \((only \text{ for } Z100)\) can suggest that the primary particles are single crystals as seen with Tani et al. For Z40, existence of the large particles can decrease the SSA and the low flame temperature may suppress the crystal growth. However, it is still unknown why the \(d_{\text{BET}}\) and \(d_{\text{XRD}}\) were not changed so much among Z100, Z80 and Z60 in spite of the different flame temperatures. On the other hand, the \(d_{\text{BET}}, d_{\text{XRD}}\) and \(d_{\text{TEM}}\) were not consistent with each other for the MgO synthesis. The hydroxylation decreases the solid density \((\text{MgO}: 3.6 \text{--} \text{Mg}(\text{OH})_2: 2.37 \text{ Mg/m}^3)\) and may increase the SSA for M100 judging from the result that the SSA increased significantly for M60 where hydroxylation can be enhanced, resulting in the smaller \(d_{\text{BET}}\) than \(d_{\text{TEM}}\). The crystallinity of the MgO particles may decrease also by hydroxylation, broadening the XRD peaks, resulting in the smaller \(d_{\text{XRD}}\) than \(d_{\text{BET}}\) and \(d_{\text{TEM}}\).

5. Summary

Polyhedral aggregates of nanoparticles were made by FSP using the solvents with methanol content of ≥0.6 for both ZnO and MgO synthesis, suggesting complete evaporation of the metal species in the flame and particle formation in the gas phase, whereas using the solvent with methanol content of 0.4 suppressed the evaporation, leading to particle formation both in the gas and liquid phases, resulting in a mixture of nanoparticles and large particles also for both cases. The criteria for the complete evaporation were not changed in these experimental conditions for ZnO and MgO synthesis in spite of the different physical properties of these oxides as well as their precursors.

The XRD and IR spectra showed hydroxylation of MgO during the FSP process, which can be explained by the larger Gibbs energy change for hydroxylation in MgO than in ZnO. The \(d_{\text{BET}}, d_{\text{XRD}}\) and \(d_{\text{TEM}}\) \((only \text{ for } Z100)\) were in agreement with each other for Z100, Z80 and Z60, suggesting single crystalline primary particles, whereas the \(d_{\text{BET}}, d_{\text{XRD}}\) and \(d_{\text{TEM}}\) \((only \text{ for } Z100)\) were not consistent for M100, M80 and M60. Hydroxylation of MgO may influence the product particle characteristics.

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References