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A new technique for preparing ceramics for catalyst support exhibiting high porosity and high heat resistance

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Abstract

A new technique for preparing magnesia ceramics of high porosity and high temperature resistance has been developed. Spray freeze drying of magnesium sulfate aqueous solution produced fine salt particles having open pores due to sublimation of ice crystals. The particles were calcined to porous magnesium oxide and formed a green body. Highly porous magnesia was produced by firing the green body. The porous magnesia exhibited a bimodal pore size distribution of macro-pores of micron order and meso-pores smaller than 100 nm. Porosity was 87–90%. After addition of an aluminum additive with an amount 3–5 mol%, the magnesia exhibited high heat resistance; surface area was greater than 20 $m^2\ g^{-1}$ after 20 h exposure in a 1573 K oven. Thus, the porous magnesia is expected to be very suitable for combustion catalyst support used in a high temperature environment.

Keywords: Catalyst support; High heat resistance; High porosity; Freeze drying

1. Introduction

Porous ceramics of open-cell structure have been used in a wide range of applications, such as molten-metal filters, diesel engine exhaust filters, industrial hot-gas filters, and catalyst supports. In the present study, a novel technique based on freeze drying has been developed for producing high porosity, high heat resistance ceramics. High porosity ceramics having open pores are considered suitable for catalyst supports, because of low mass transfer resistance. High heat resistance is a property required of combustion catalyst supports, especially for application in a high temperature range. Stabilized alumina-added La and/or Ba added to alumina matrix [1–3] and Si-stabilized alumina [4] have been developed as inexpensive, stable, and durable support materials. Such a support can withstand continuous operation at temperatures between 1200 and 1300 K without excessive sintering.

In this study magnesia was selected as base material, because it exhibits no crystal phase change at high temperature. Addition of a second metal to the bulk magnesia to suppress sintering was examined. The porous magnesia was made of porous particles prepared by freeze drying.

Freeze dry processing was first applied to ceramics powder preparation by Schnettler et al. [5]. Yokota and Ohto [6] developed a wetted-column-type freezer for a spray freeze dry method which can produce fine porous particles. In their method, metal salt porous particles are calcined into porous oxide particles. By forming the oxide particles into a green body and firing it, a high porosity ceramic having open pores can be produced.

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2. Experimental

Magnesium sulfate aqueous solution (2 mol dm^{-3}) was prepared as a starting feed solution for freeze dry processing. The solution was sprayed through a two-fluid nozzle running nitrogen gas in a wetted wall-column freezer [6]. Fine droplets of the aqueous solution were trapped by a refrigeration agent of *n*-hexane cooled at 213 K, and solidified instantaneously into frozen particles. Average diameter of the frozen particles was 42 μm. The frozen particles were transferred into a vacuum chamber, and its temperature was controlled so as to sublimate the ice crystals. The traces of the sublimation inside the dried particles became open pores having a diameter of the micron order.

The dried particles were calcined into magnesium oxide in a tubular-type oven. The rate of temperature increase (10 K min^{-1}), the highest temperature attained (1473 K), and the vacuum atmosphere within the oven were selected in order to attain large surface area in a porous particle.

The porous oxide particles were formed to a cylindrical green body of 10 mm diameter and 3 mm thickness, using ethyl alcohol (8×10^{-3} dm^3 per 1 g oxide particle) as the binder. A rather low compression pressure (1.25 MPa) was used in the formation, so as to not crush the pores in oxide particles and to obtain a green body of uniform cylindrical structure.

Firing of the green body was carried out in an oven containing an air atmosphere. The rate of temperature increase was 10 K min^{-1}, and the attained temperatures were controlled within a range 1573–1773 K. In order to test heat resistance, the fired bodies were set in an oven of 1573 K and held in the oven for up to 20 h. The effect of water vapor on sintering was also examined in a tubular oven through which humidified air flowed.

A second metal was added in order to suppress sintering of the magnesia, so as to obtain a durable combustion catalyst support. Aluminum, zinc, and chromium metals were used as the additive. A certain volume of the additive metal sulfate solution was added to the feed of magnesium sulfate aqueous solution. The two metal components were well mixed in the feed solution and instantaneously solidified in the freezer without segregation. The mixed frozen particles were treated in the same manner described above in order to obtain porous magnesia with another metal component.

For characterization, the porous materials were subjected to SEM observation (Nihon Denshi, JSM-T330), measurement of porosity, pore volume, and pore size distribution (Yuasa-Ionics, ASP 60), specific surface area (by the BET method), and X-ray diffraction pattern analysis (Shimadzu, XD-D1).

3. Results and discussion

Fig. 1 shows SEM micrographs of the freeze-dried and calcined particles. Spray freeze-dried particles

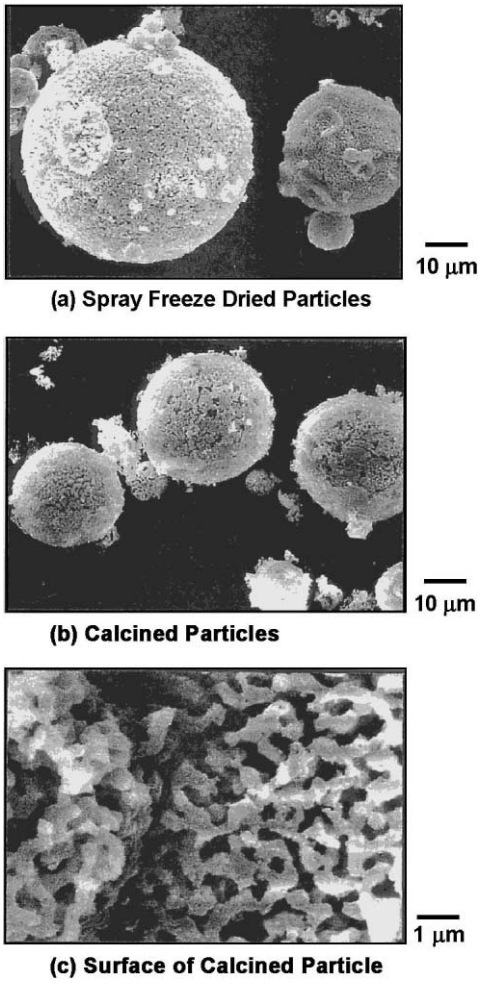

Fig. 1. SEM observation of spray freeze-dried magnesium sulfate particles and calcined magnesium oxide particles.

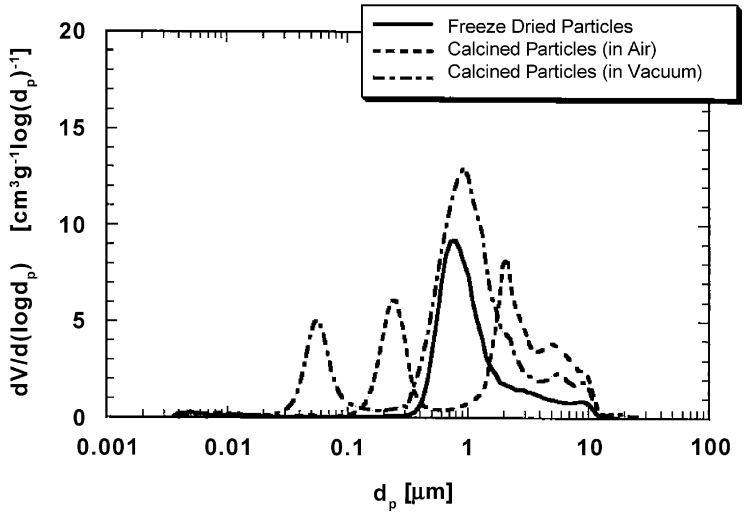

Fig. 2. Pore size distributions of freeze-dried magnesium sulfate particles and calcined magnesium oxide particles.

were porous spheres, and their average diameter was 42 μm. Calcined particles also retained a spherical shape, but their size was reduced to an average diameter of 20 μm. The porous structure in the particles still remained.

Fig. 2 shows the pore size distributions as measured by a mercury porosimeter. The freeze-dried particles contain, as main pores, macro-pores in the order of 1 μm formed through ice crystal sublimation. The calcined particles show a bimodal pore distribution. The macro-pores are from the dried particle pores, and other pores of sub-micron scale appeared after thermal decomposition of metal sulfate salt into metal oxide. Micro-pores formed through SO_x gas ejection must have enlarged into meso-pores during the calcination process. Particles calcined in air contain larger macro- and meso-pores as compared with those calcined in vacuum. SO_x gas ejected by thermal decomposition of sulfate is easily evacuated from particles in vacuum. In air, SO_x gas might expand pores before escaping from particles. The smaller meso-pores contribute to the large surface area of MgO particles. Thus, the particles calcined in vacuum were used for forming green bodies.

Cylindrical green body samples were fired in an oven controlled within a range 1573–1773 K. In order to examine heat stability, the fired samples were placed in an oven controlled to 1573 K and held therein for several hours. Fig. 3 shows the change in specific surface area as a function of holding time. In the figure, "fresh sample" means one that has not been subjected to a stability test. The results indicate that considerable sintering occurred for these samples. In most of the samples, surface area was reduced to about 10 $m^2\,g^{-1}$ after a 3 h test.

A second metal was added to magnesia in an effort to attain high heat resistance. The aluminum additive worked effectively to suppress sintering. Fig. 4 illustrates the relationship between specific surface area and holding time, and that between porosity and holding time for samples with 3, 5 mol% aluminum additive fired at 1573 K. The samples exhibit fairly high surface area above 20 $m^2\,g^{-1}$ and high porosity above 86% even after 20 h exposure in an oven maintained at 1573 K. In humidified air, the samples with aluminum additive show high heat stability. The samples of 1 mol% aluminum content show smaller surface areas than do those displayed above, and 10 mol% content samples show almost the same heat-resistance as illustrated in Fig. 4.

The X-ray diffraction pattern of the magnesia sample with aluminum additive shows small $MgAl_2O_4$ spinel peaks among the MgO peaks. When the spinel phase was formed at grain boundary of bulk magnesia, this second boundary phase impeded diffusion of bulk atom and prevented grain growth. Thus, the

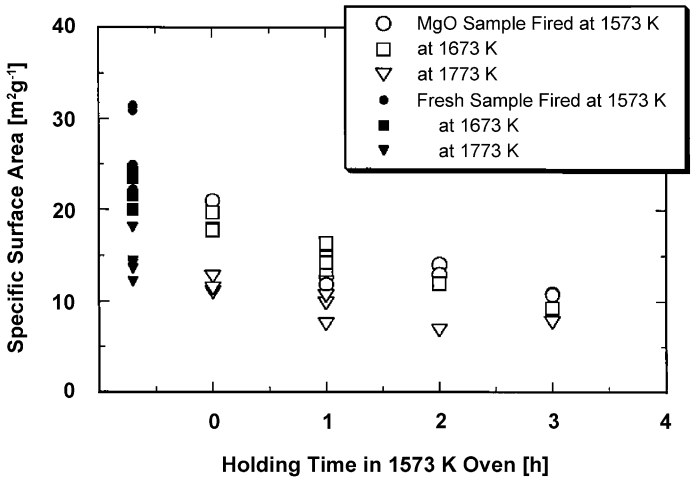

Fig. 3. Relationship between specific surface area and holding time in a 1573 K oven for magnesia samples without the second metal additive.

magnesia with aluminum additive exhibits high heat resistance.

The effect of zinc metal additive was examined, but heat stability was not improved. The change in surface area as a function of holding time in the oven is almost the same as that shown in Fig. 3. Zinc metal does not form a spinel compound with magnesium. Therefore, zinc atoms fused in bulk magnesia formed a solid

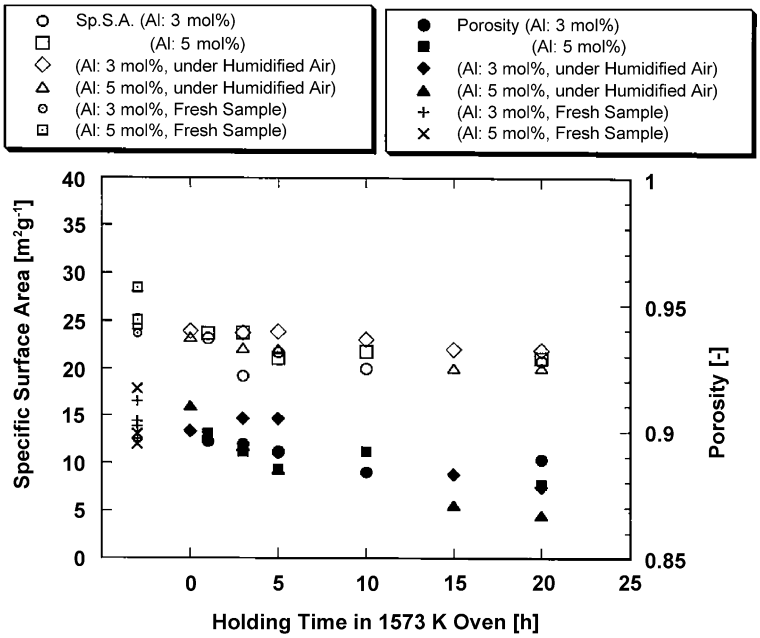

Fig. 4. Relationship between specific surface area, porosity and holding time in a 1573 K oven for magnesia samples with aluminum additive.

solution. When chromium metal was added in magnesia, the fresh sample exhibited small surface area; i.e., below $10\,m^2\,g^{-1}$. Therefore, further heat stability testing was not carried out.

4. Conclusions

Porous heat-stable magnesia was prepared from porous MgO particles produced by spray freeze drying. The magnesia shows a bimodal pore size distribution of macro-pores in the order of microns and meso-pores under 100 nm. Porosity was 87–90%. The magnesia with 3–5 mol% aluminum additive exhibits high heat resistance, with specific surface area being greater than $20\,m^2\,g^{-1}$ after 20 h exposure in a 1573 K oven. Thus, the magnesia is expected to be very suitable for combustion catalyst support used in a high temperature operation.

Acknowledgements

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