Fractal Surfaces of ZrO₂, WO₃, and CeO₂ Powders

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Abstract—The surface fractal properties of ZrO_2 , WO_3 , and CeO_2 powders prepared by the thermal decomposition of $ZrO(NO_3)_2$, $(NH_4)_4W_5O_{17}$, and $(NH_4)_2Ce(NO_3)_6$, respectively, were studied by mercury porosimetry. The results demonstrate that these oxides may, in principle, have fractal surfaces owing to topochemical processes of the type $A(s) \longrightarrow B(s) + C(g)$. The surface fractal dimension of individual crystallites and their aggregates are determined.

INTRODUCTION

Earlier results on the surface structure of Fe_2O_3 powders differing in thermal history suggest that, when conducted under relatively mild conditions to avoid defect annealing and grain growth, the decomposition of metal salts accompanied by gas release may yield oxide powders with fractal surfaces [1]. To verify this assumption, we studied the surface fractal structure of ZrO₂, CeO₂, and WO₃ powders prepared by decomposing ZrO(NO₃)₂, (NH₄)₄W₅O₁₇, and (NH₄)₂Ce(NO₃)₆, respectively.

EXPERIMENTAL

 ZrO_2 samples were prepared by heating crystalline, reagent-grade $ZrO(NO_3)_2$ to 315°C at 5°C/min, followed by isothermal holding for 3 h.

WO₃ samples were prepared by heating crystalline, reagent-grade $(NH_4)_4W_5O_{17}$ to 580°C at 5°C/min, followed by isothermal holding for 3 h.

CeO₂ samples were prepared by heating crystalline, reagent-grade $(NH_4)_2Ce(NO_3)_6$ to 315°C at 5°C/min, followed by isothermal holding for 3 h.

The powders were characterized by x-ray diffraction (XRD) on a DRON-3M diffractometer (Cu K_{α} radiation) at a scan rate of 1–2°/min. The results were analyzed using JCPDS Powder Diffraction File (PDF2) data.

Microstructures were examined by scanning electron microscopy (SEM) on a JEOL JEM-2000FXII instrument (accelerating voltage, 200 kV; magnifications, up to $\times 20000$).

The porosity of preevacuated (1.3 Pa) samples was determined by Hg intrusion porosimetry at pressures from 0.3 to 220 MPa (Micromeritics PoreSizer 9300). Cumulative and differential pore size distributions and specific surface areas were found by analyzing the intrusion curve under the assumption that the pores had a cylindrical shape. The contact angle between mercury and the material was assumed to be 130°.

The fractal dimension D of the ZrO_2 , CeO_2 , and WO_3 powders was extracted from Hg porosimetry data using the Neimark formula [2]

$$D = 2 + d \left(\log \int_{0}^{V} p \, dV \right) / d(\log p)$$

$$= 2 + d (\log f(p)) / d(\log p),$$
(1)

where *V* is the Hg intrusion volume, *p* is the applied pressure, and $f(p) = \int_0^V p \, dV$.

RESULTS AND DISCUSSION

According to XRD and Hg porosimetry data, the thermal decomposition of zirconyl nitrate and ammonium cerium nitrate at 315°C yields single-phase ZrO₂ and CeO₂ powders characterized by a high porosity and specific surface (table; Figs. 1b, 1c). The WO₃ powders obtained at a higher temperature (580°C) have a smaller specific surface and a lower percentage of small ($d < 0.03 \mu$ m) pores (Fig. 1a). Clearly, high-temperature defect annealing has a profound effect on the microstructure of the materials.

An analysis of the Hg intrusion curves with the use of the Neimark equation indicates that the WO₃ powder has a fractal surface with a fractal dimension $D = 3.00 \pm$ 0.02 (Fig. 2a), which is characteristic of the pore structure of loose aggregates consisting of weakly bonded oxide particles [1]. The same is evidenced by the limits of the self-similarity range: 0.11 to 1.15 µm.

Fractal analysis of the curves obtained for zirconia powders reveals two distinct linear portions (d = 0.14-0.77 and 0.02–0.14 µm) with slopes corresponding to

log f(p)

4.5

4.0

3.5 3.0

2.5

2.0

4.4

4.2 4.0

3.8

3.6

3.4

4.5

4.2

3.9

3.6

3.3

0.4

0.4

0.4

0.8

0.8

0.8



Fig. 1. Pore size distributions of (a) WO_3 , (b) ZrO_2 , and (c) CeO_2 samples.

fractal dimensions of 3.03 ± 0.04 and 2.31 ± 0.02 (Fig. 2b). As in the case of WO₃, the former portion corresponds to the fractal dimension of the pore structure of zirconia aggregates, while the latter characterizes the topology of the pore structure of the particles, which has a smaller fractal dimension. These conclusions are supported indirectly by the SEM micrographs



(a)

(b)

1.2

1.2

1.2

(c)

1.6

1.6

1.6

of the ZrO_2 powders (Fig. 3), which demonstrate that the particles range in size from 0.2 to 3 μ m.

The CeO₂ powder, prepared by the thermal decomposition of crystalline ammonium cerium nitrate, exhibits surface fractal properties only in a relatively narrow range of pore sizes, from 0.16 to 0.6 μ m, which corresponds, according to SEM data (Fig. 4), to inter-

Sample	$V_{\rm sp},{\rm cm^3/g}$	$S_{\rm sp},{\rm m^2/g}$	$\Delta d, \mu m$	Self-similarity range, µm	D
CeO ₂	2.0	33.3	0.03–0.9	0.16–0.6	2.84 ± 0.01
ZrO ₂	0.9	52.0	0.0088-1.3	0.02–0.14	2.31 ± 0.02
				0.14-0.77	3.03 ± 0.04
WO ₃	0.1	8.8	0.016-1.15	0.11-1.15	3.00 ± 0.02
Fe ₂ O ₃ [1]	2.1	-	0.02–2.3	0.02-0.19	2.42 ± 0.04
				0.19–2.3	3.01 ± 0.03

Mercury porosimetry data for ZrO₂, WO₃, and CeO₂ powders

Note: V_{sp} is the specific pore volume, S_{sp} is the specific surface area, Δd is the spread of pore sizes, and D is the fractal dimension.



Fig. 3. SEM micrographs of zirconia powders: (a) \times 5000, (b) \times 20000.

aggregate pores. The fractal dimension of the pore surfaces is 2.84 ± 0.01 (Fig. 2c). The log–log plot of the Neimark function is nonlinear at high pressures (above 10 MPa), indicating that the surface of individual CeO₂ particles has a nonfractal topology.

Comparison of the surface fractal properties of ZrO_2 , CeO_2 , and WO_3 powders with those of Fe_2O_3 [1] indicates that all these powders have morphologically inhomogeneous structures. In view of this, it is reasonable to distinguish two levels of microstructural organization, similarly to the classification proposed earlier [3, 4]. The first level corresponds to primary oxide crystallites. The porosity at this level is due to intercrystalline pores ($d < 0.1 \ \mu m$) comparable in size to the primary crystallites. The second level corresponds to



Fig. 4. SEM micrographs of ceria powders: (a) $\times 10000$, (b) $\times 50000$.

aggregates of primary crystallites and their agglomerates. The interaggregate pores are close in size to the aggregates (0.2 to 2 μ m and larger).

Note that, at the first level of this hierarchy, the fractal dimension of the pore structure depends on the synthesis and sintering conditions and varies from ~2.6 to 2 (absence of fractal properties owing to annealing processes). In a number of samples, the fractal dimension of the pore structure of aggregates is D = 3, which points to the maximum morphological inhomogeneity. If the synthesis conditions are such that the dimension of the pore structure of aggregates is between 2 and 3, subsequent high-temperature sintering leads to a systematic increase in D, which gradually approaches 3.

INORGANIC MATERIALS Vol. 38 No. 12 2002

CONCLUSION

It is found that the thermal decomposition of $ZrO(NO_3)_2$, $(NH_4)_4W_5O_{17}$, and $(NH_4)_2Ce(NO_3)_6$ under conditions that prevent defect annealing and crystallite sintering, yields ZrO_2 , WO_3 , and CeO_2 powders with fractal surfaces. Such powders are characterized by two levels of microstructural organization. The surface fractal dimension of the pore structure of aggregates notably exceeds the fractal dimension of intercrystalline pores and occasionally attains D = 3, a value characteristic of very rough surfaces.

ACKNOWLEDGMENTS

This work was supported by the Leading Scientific Schools Program, grant no. 00-15-97435.

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