ESR Characterization of ZrO_2 Nanopowder

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ESR techniques have been used to study ZrO_2 nanopowder (10−100 nm particle size) prepared by precipitation methods. They show that nano-ZrO_2 has two kinds of ESR signals, which are assigned to Zr^{3+} and F-center paramagnetic centers, respectively. The Zr^{3+} signal is a bulk related signal; on the contrary, the F-center signal is surface related. Quantitative ESR experiments indicated that the F-center signal intensity increases and the Zr^{3+} signal intensity decreases with the increase of specific surface area: 50 nm is a critical particle size; when the nanoparticle size is bigger than 50 nm, its F-center signal vanishes, but its Zr^{3+} signal intensity increases dramatically.

Introduction

The study of ZrO_2 has attracted considerable attention because of its various important applications. In the past several years, a flourish of activity on research directed toward synthesizing ZrO_2 with nanoscale dimensions has taken place, in order to prepare extremely small crystallite size powder with a narrow size distribution.[1−3]

Although electron spin resonance (ESR) properties of nano-sized clusters of metals has been investigated extensively in recent years,[4,5] there is only one preliminary report about the ESR properties of nano-ZrO_2 prepared by the explosion technique to our knowledge.[6] The ESR characteristics of ZrO_2 are firmly related to its reactivity with water and CO,[7] while these reactions have important influence on the catalytic, electronic, and tribological properties of zirconia.

This paper is concerned with reporting the ESR properties of nanozirconia. The characteristics of ESR signals are discussed in terms of the observed particle size effect, which appears to be a critical factor governing the changing of the ESR signals.

Experimental Section

$ZrOCl_2{\cdot}8H_2O$ (2 mol) was dissolved in distilled water. To this clear aqueous ammonia was added dropwise until complete precipitation of $Zr(OH)_4$ took place, when the pH value of the solution was larger than 7. The precipitate was dried at 100 °C. The powders were calcined for 1 h at different temperatures varying from 500 to 1200 °C in air followed by the natural cooling in the furnace. The specific surface area of the powder was measured by the BET method.[8] The BET measurement was conducted using a Sorptomatic 1800 instrument (Carlo ERBA Corp., Italy). The error associated with BET surface area measurement is within ±2%. The particle size was measured by transmission electron microscopy (TEM). An X-ray diffractometer (XRD) with graphite-filtered Cu Kα radiation was used to determine the phase present in the calcined powder over 2θ values from 20° to 80°. Crystallite size was calculated using the $(202)_T$ and $(111)_m$ diffraction peaks from the Scherrer formula as shown here:[9]

$$D = 0.9\lambda/\beta \cos\theta$$

where D is the crystallite size in nm, λ is the radiation wavelength (0.154 nm for Cu Kα radiation), β is the corrected half-width of the peak profile, and θ is the diffraction peak angle. The composition of nano ZrO_2 powder was determined by X-ray photoelectron spectroscopy.

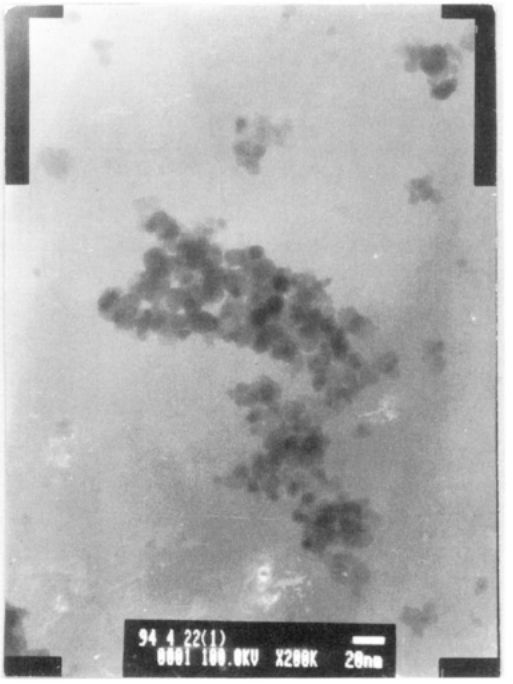

Figure 1. TEM photomicrograph of ZrO_2 powder calcined at 500 °C for 1 h.

ESR spectra were recorded at room temperature in air with a Varian E-115 spectrometer operating in the X band (ν = 9.2 GHz) with 100-kHz field modulation. The nano-ZrO_2 powder was used as a loose powder for the ESR measurement. In this study we had not found any apparent influence of oxygen on the ESR signals. ESR parameters were calibrated by comparison with a standard Mn^{2+}/ZnS (the distance between its first and sixth line is 34.05 mT) and 2,2-diphenyl-1-picrylhydrazyl (DPPH, g = 2.0036). The number of spins per gram was determined by comparing the signal area of the sample with that of DPPH (9.7×10^{15} spins).

Results and Discussion

Characteristics of the ZrO_2 Nanopowder. A TEM photomicrograph of ZrO_2 powders calcined at 500 °C is shown in Figure 1. Particles having a size of ~10 nm are visible in the

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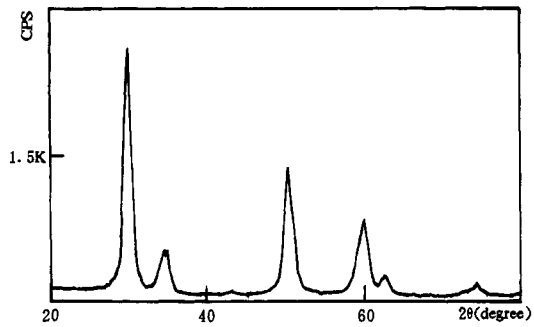

Figure 2. XRD pattern of ZrO_2 nanopowder calcined at 500 °C for 1 h.

TABLE 1: Characteristics of the ZrO_2 Powders Calcined for 1 h at Different Temperatures[a]

sample	T_{cal} [°C]	S_{BET} [m^2/g]	D_{XRLB} [nm]	P_{TEM} [nm]	phase	color
W1	500	74	9.5	10	T	brown
W2	700	33	11.0	15	T + m	yellowish
W3	900	16	24.9	50	M + t	white
W4	1000	4	27.6	86	M	white
W5	1200	3	35.4	100	M	white

[a] T_{cal}, temperature of calcination; S_{BET} specific surface area; D_{XRLB}, crystallite size determined by X-ray line broadening; P_{TEM}, particle size as determined by TEM; T, tetragonal phase; M, monoclinic phase; T + m, mostly in the tetragonal phase, but there exists some monoclinic phase; M + t: mostly in the monoclinic phase, but a small amount of tetragonal phase remains.

powders. XRD analysis of these powders indicated that the as-prepared powders exhibit the tetragonal ZrO_2 phase. The XRD spectrum is shown in Figure 2.

The characteristics of all five prepared powders are summarized in Table 1. XRD analysis showed that all powders are crystalline, and the phase of ZrO_2 nanopowder transforms from tetragonal to monoclinic when the calcination temperature is increased from 500 to 1200 °C. Table 1 indicates that the crystalline size (D_{XRLB}) and particle size (P_{TEM}) increase with increasing calcination temperature, while the specific surface area (S_{BET}) changes in reverse. Furthermore, the color of the powders is different, which is shown in Table 1.

Formation of the Paramagnetic Centers. The ESR measurements of the samples calcined at different temperatures as listed in Table 1 revealed that all the samples have ESR signals. Typical spectra are shown in Figure 3. Spectrum a is composed of a strong isotropic ESR signal (I) and a weak axially symmetric signal (II). When the sample was calcined at ≥900 °C, signal I vanished and signal II became stronger (see spectra b and c). Correlating the variations of signals I and II with the change of S_{BET} (see Table 1), we suggest that signal I is surface related, while signal II is bulk related.

To understand the formation of the paramagnetic centers in nano-ZrO_2, XPS composition analysis was performed. The ratio between O and Zr is about 1.7:1, which indicates that nano-ZrO_2 has a lot of oxygen vacancies.[10] When the particles are very small, we have to consider their surface effects, as the atoms distributed on the surface are more than 50% of the total atoms.[11,12] Therefore, the oxygen vacancies of ZrO_2 nanopowder can be divided into two parts. One of them is located in the bulk of the material, while the other is located on the surface. The surface vacancies are so active that electrons can be trapped.[6,11] When a single electron is captured at the surface oxygen vacancy, F-centers are formed, corresponding to the isotropic signal I at $g = 2.003$. The bulk Zr^{4+} ions which are adjacent to the bulk oxygen vacancies could capture electrons

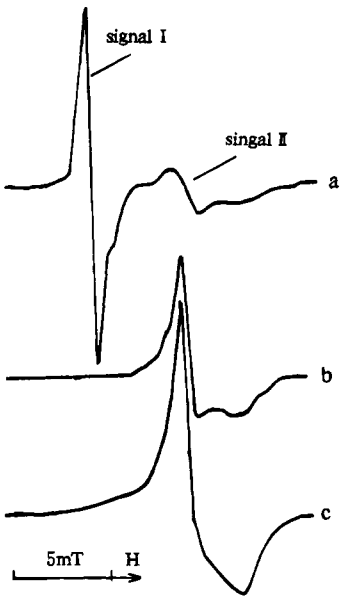

Figure 3. ESR spectra of nano-ZrO_2: (a) calcined at 500 °C (W1); (b) calcined at 900 °C (W3); (c) calcined at 1200 °C (W5).

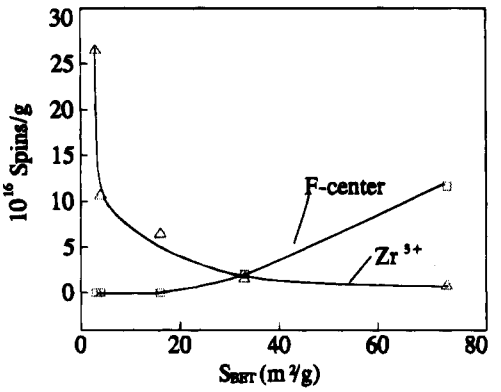

Figure 4. Variation of Zr^{3+} and F-center ESR signal intensities as a function of S_{BET}.

resulting in the formation of Zr^{3+} ions. Signal II, at $g_\perp = 1.974$, $g_\parallel = 1.961$, is probably contributed by the bulk Zr^{3+} ions located at axially symmetric sites (see Figure 3).[6,7,10]

Effect of Particle Size on the ESR Signal. The variation of Zr^{3+} and F-center signals as a function of BET specific surface area (S_{BET}) is plotted in Figure 4. It is evident that the intensity of F-center signal increases and the intensity of Zr^{3+} signal decreases with the increase of specific surface area. The increase of S_{BET} enhanced the surface effect of nano-ZrO_2 because the percentage of surface atoms was increased. So the surface related F-center signal intensity increases with increasing S_{BET}, while the bulk related Zr^{3+} signal becomes weaker. It can be seen from Figure 4 that S_{BET} has a critical value of 16 m^2/g. When the S_{BET} value is smaller than 16 m^2/g, the F-center signal vanishes, while on the contrary, the Zr^{3+} signal increases very sharply. This means that the surface signal can be neglected, and the ESR signal exhibits bulk properties. Comparing Figure 4 with Table 1, we can conclude that the critical particle size for nano-ZrO_2 is 50 nm. These results are in favor of the proposed assignment about the formation of the Zr^{3+} and F-center paramagnetic centers.

Relationship between Crystallite Size and F-Center Signal. The characteristics of ZrO_2 nanopowder calcined at 500 °C for different durations are listed in Table 2. XRD analyses show that when the calcination time varied from 1 to 5.5 h, the crystallite size of these samples remains 9.5 nm and it remains

TABLE 2: Characteristics of the ZrO_2 Powders Calcined at 500 °C for Different Durations (All in the Tetragonal Phase)[a]

sample	t_{cal} [h]	S_{BET} [m^2/g]	D_{XRLB} [nm]
W6	1	74	9.5
W7	2	58	9.5
W8	3	53	9.5
W9	4.5	50	9.5
W10	5.5	47	9.5

[a] t_{cal}, duration of calcination; S_{BET}, BET specific surface area; D_{XRLB}, crystallite size determined by X-ray line broadening.

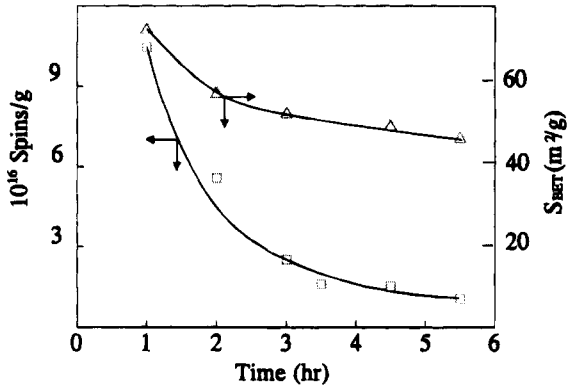

Figure 5. Variation of S_{BET} and F-center ESR signal intensities of the samples calcined at 500 °C as a function of calcining time.

in the tetragonal phase. However, their S_{BET} decreases from 74 to 47 m^2/g. This may be caused by the aggregation of the crystallites. The relationship between specific surface area, F-center signal intensity, and calcination time is given in Figure 5. The F-center ESR signal intensity increases dramatically from 1.2×10^{16} to 11.6×10^{16} spins/g while the S_{BET} increases from 47 to 74 m^2/g. These results clearly indicate that the F-center ESR signal is closely related to the S_{BET} value or particle size rather than the crystallite size.

Conclusion

Nano-ZrO_2 has two kinds of ESR signals. They can be assigned to bulk Zr^{3+} and surface F-center paramagnetic centers, respectively.

Zr^{3+} ESR signal is a bulk-related signal, while the F-center signal is surface related. Therefore, the F-center signal intensity increases with a S_{BET} increase while the Zr^{3+} signal intensity changes in reverse. The critical value of nanoparticle size above which the F-center signal is negligible is about 50 nm. Study of tetragonal nano-ZrO_2 samples indicates that their F-center ESR signal is closely related to their S_{BET} value or particle size rather than their crystallite size.

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