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Empirical Method for Determining CeO_2-Particle Size in Catalysts by Raman Spectroscopy

The addition of ceria, CeO_2, to automotive exhaust-gas catalysts has been linked to greater thermal stability of the alumina support, higher precious-metal dispersion, and wider range of parameters for three-way operation. Some, if not all, of these beneficial effects are undoubtedly influenced by the dispersion of the ceria, which is typically added at the 5–10 wt% (including the monolith) level. Methods of measuring its dispersion, or particle size, are thus important tools for studying how ceria functions.

Traditionally, either transmission electron microscopy (TEM) or X-ray diffraction (XRD) have been applied to the problem of particle size determination in catalysts. The more tedious TEM method is often used to detect particles of high-Z components that are too dilute and/or too small to be readily seen by XRD, which generally requires long data acquisition times in order to resolve the broad diffraction peaks produced by small particles. In this report, we show how Raman spectroscopy may be used to determine the size of CeO_2 particles in automotive exhaust-gas catalysts in a way that is easier than TEM and faster than XRD.

Core samples were taken from fresh catalyst monoliths of three types, A, B, and C, differentiated by manufacturer and precious-metal loading, but all containing about 6 wt% ceria. In addition, core samples of types A and B were taken from vehicle-aged (50,000 miles) catalyst monoliths. Some of the core samples from the fresh catalyst monoliths were heated in a tube furnace at 900 C for times ranging from 1 to 8 h under stoichiometric simulated exhaust gas (97.103% N_2, 1.315% O_2, 1% CO, 0.33% H_2, 0.1% C_3H_6, 0.05% C_3H_8, 0.1% NO, and 0.002% SO_2). Raman spectra were recorded from the surface of the washcoat of an exposed channel on the side of the cores, and XRD measurements were performed on powdered washcoat scraped from the corner region of an exposed channel on the side of the cores.

The Raman spectrum from the fresh type A sample is shown in Fig. 1 as a typical example. The peak at about 465 cm^{-1} is due to the Raman-active F_{2g} mode of CeO_2. By comparison with the spectrum from a single crystal of CeO_2, also shown in Fig. 1, it is evident that the Raman line in the catalyst is wider and at lower frequency than in the single crystal. From a least-squares fit of the Raman line to a Lorentzian lineshape, with a correction for instrumental broadening, the half-width at half-maximum, Γ, and frequency were derived for all the samples, as listed in Table 1. A correlation exists between the half-width and frequency, as shown in Fig. 2.

It is known that the Raman linewidth of ceria depends on temperature. Sato and Tateyama have measured the Raman spectrum of crystalline CeO_2 at temperatures ranging from 300 to 850 K and show that the increase in linewidth with temperature (by a factor of almost 3) can be explained in terms of the anharmonicity of the crystal potential energy (*1*). Since the catalyst

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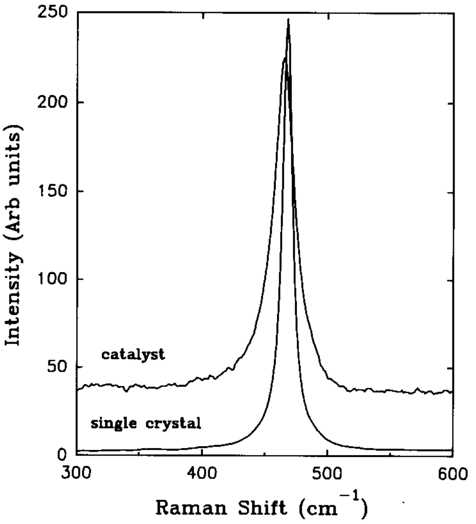

FIG. 1. Raman spectra of CeO_2 from the fresh type A catalyst and a single crystal recorded with the 514.5-nm line from an Ar laser using an array detector system. Experimental conditions: 100 × 250-μm spot, 1.8-mW power and 9-min exposure for the catalyst, and 50-mW power and 6-min exposure for the single crystal. The signal from the catalyst has been multiplied by a factor of 40.

samples are opaque, this sort of thermal broadening could easily be induced by laser heating. By measuring the dependence of the Raman linewidth on laser power, however, we became satisfied that this effect could be made negligible at a power level of 1–2 mW.

Another explanation for the variation in Raman linewidth and frequency, previously suggested by Shyu *et al.* in their study of alumina-supported ceria (*2*), has to do with the size of the CeO_2 particles. In an infinite crystal, momentum conservation limits the first-order Raman-scattering processes to the zone-center ($q = 0$) optical phonons. In a particle of size D, momentum conservation is partially relaxed, and phonons of wavevectors extending from zero to $|q| \sim 1/D$ can contribute to the scattering. The F_{2g} mode in CeO_2, which is triply degenerate at $q = 0$, splits and shifts to both higher and lower frequency away from $q = 0$. Thus a broadened (and possibly shifted) lineshape should result. A spatial correlation model of this effect has been used to account for the variations in Raman linewidth and frequency observed in microcrystalline Si by Richter *et al.* (*3*) and in ion-implanted GaAs by Tiong *et al.* (*4*). There should be a specific relationship between linewidth and frequency according to this model, but we have so far not made a serious attempt to apply it to the case of ceria. Instead, we have plotted the half-width as a function of inverse CeO_2-particle size, derived by applying the Scherrer relation to the (111), (200), (220), and (311) XRD lines, and obtain the result shown in Fig. 3. Clearly, there is a strong correlation between the Raman linewidth and inverse particle size, and the dashed line in this figure is a least-squares fit yielding the relation $\Gamma(\mathrm{cm}^{-1}) = 5.26 + 436/D(\text{Å})$.

Taken at face value, Fig. 3 can be used to empirically determine CeO_2-particle size in

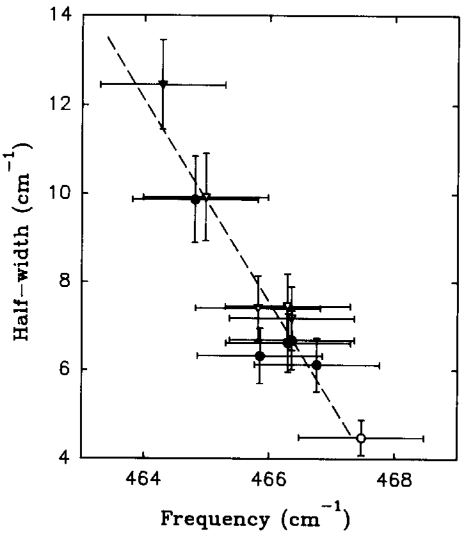

FIG. 2. Half-width of the Raman line as a function of frequency for all the CeO_2 samples listed in Table 1. The filled inverted triangle is from the type C catalyst, the open inverted triangles are from the type B catalysts, the filled circles are from the type A catalysts, and the open circle is from the single crystal. The dashed line is a guide to the eye.

TABLE 1

Results of Raman and XRD Analyses of CeO_2 Samples

Sample	Raman results		XRD results
	Raman frequency (cm^{-1})	Half-width, Γ (cm^{-1})	D (Å)
	Type A		
Fresh	464.81 ± 1.00	9.87 ± 10%	94 ± 26
50K miles	466.30	6.61	456 ± 200
900°C, 1 h	466.36	6.68	323 ± 24
900°C, 4 h	465.85	6.32	441 ± 38
900°C, 8 h	466.76	6.12	337 ± 34
	Type B		
Fresh	464.98	9.92	91 ± 12
50k miles	466.29	7.44	178 ± 23
900°C, 1 h	466.36	7.17	301 ± 22
900°C, 4 h	465.82	7.40	296 ± 47
	Type C		
Fresh	464.29	12.45	60 ± 12
Single crystal	467.47	4.48	∞

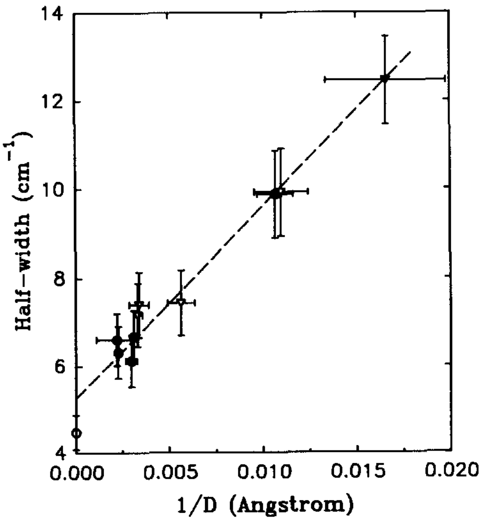

FIG. 3. Half-width of the Raman line as a function of inverse particle size for all the CeO_2 samples. The symbols are as defined in Fig. 2. The dashed line is a linear least-squares fit as described in the text.

catalysts by Raman spectroscopy. Compared with the XRD measurements needed to construct Fig. 3, the corresponding Raman spectra were obtained in about one-tenth the time. In applying the Raman method, however, it is important to take into account the influence of laser-induced thermal broadening. This, and possibly other factors not considered, such as defects in the CeO_2 lattice, may affect the details, if not the functional form, of the relation depicted in Fig. 3. Systematic studies, performed on well-characterized samples, could be done in order to further test and refine the basic correlation observed between Raman linewidth and XRD line broadening.

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