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Cerium Dioxide Crystallite Sizes by Temperature-Programmed Reduction

Yao and Yao recently reported (*1*) that the temperature-programmed reduction (TPR) traces of unsupported ceria show two peaks, which are associated with surface capping oxide ions and bulk ions, respectively. The work reported here has confirmed their qualitative relationship between the magnitude of the "capping oxide" peak and BET surface areas of the ceria specimens. Furthermore, the observed quantity of hydrogen consumed in reducing the capping oxygen is in good agreement with values predicted from surface area, using a simple cubic model. This finding makes it possible to determine the specific surface area of supported ceria. By extension, this method can be applied to other supported reducible oxides.

The BET nitrogen adsorption technique is by far the most common method for determining the degree of subdivision of a solid material. In some circumstances, however, it becomes desirable or necessary to use other techniques, such as measurement of an average crystallite size by broadening of an X-ray diffraction (XRD) peak. This is particularly true when the compound of interest is only one component of a catalyst, for example, when a support is the major component. In the present work, the line-broadening results for three cerium dioxide specimens are in relatively poor agreement with crystallite sizes calculated from the BET areas, using the same cubic model. Clearly, since the XRD line broadening in these cases is due to factors besides crystallite size, the TPR technique is a superior method for examining supported metal oxides.

EXPERIMENTAL

Three samples of pure cerium dioxide were used for this work. The first two were C.P. grade purchased from Fisher Scientific: Sample I in 1974 and Sample II in 1983. Sample III was obtained from cerium nitrate by precipitation with ammonia and subsequent calcination at 550°C. Two separate calcinations of one precipitated product were combined to produce Sample III.

Surface areas were measured with a Micromeritics Model 2500 analyzer. X-ray diffractions were obtained with a Norelco diffractometer using Cu$K\alpha$ radiation, with an on-line Apple computer to store the data and to calculate half-widths. The measurements were made using the strongest XRD line at 28.6° (2θ) (111). Corrections for machine broadening were made by the usual method:

$$W_{1/2} = (B^2 - b^2)/B^2, \qquad (1)$$

where B = full-width at half maximum (specimen); b = full-width at half maximum (machine).

The crystallite size (d) is, therefore,

$$d = (0.9)(57.3)(\gamma)/W_{1/2} \cos \theta \quad (\text{in Å}), \qquad (2)$$

where γ = X-ray wavelength = 1.7418 Å; θ = diffraction angle.

Temperature-programmed reduction (TPR) runs were made by a method essentially described by McNicol (*2*). A blend of 5.12% hydrogen in nitrogen was passed at 50 ml/min through 0.14–1.0 g of sample in a U-tube sample holder while the sample was heated at a constant rate of 15°C/min to about 900°C. The effluent stream was moni-

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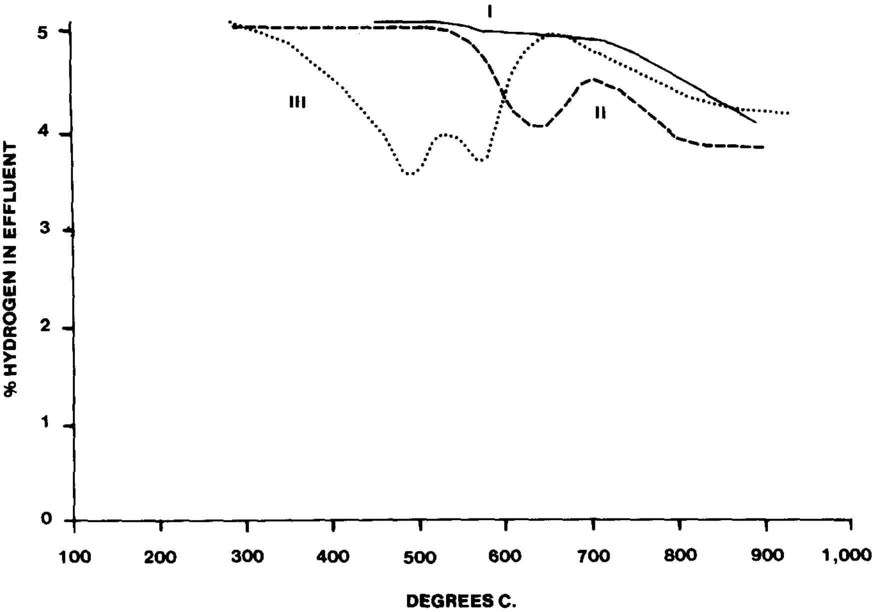

FIG. 1. TPR runs with cerium dioxide. I, 0.7 m^2/g; II, 13 m^2/g; III, 27 m^2/g.

tored for hydrogen, after removal of moisture in a dry-ice trap, by a thermal conductivity system. The digitized time vs percentage hydrogen loss data were integrated to the zero base lines, on a computer, in order to obtain hydrogen consumption data. The first (capping) peaks were defined by the minimum before the major peaks. The data were converted to plots of temperature vs percentage hydrogen in effluent by computer. These plots are shown in Fig. 1.

TABLE 1

Cerium Dioxide

Sample	Area (m^2/g)	Hydrogen consumed		
		Total H/Ce	Capping H_c/Ce	
			Observed	Predicted
I	0.7	0.30	0.005	0.006
II	13	0.39	0.102	0.103
II	13	0.49	0.108	0.103
II	13	0.39	0.096	0.103
III	27	0.35	0.141	0.212

RESULTS

The surface area, hydrogen consumption, and XRD crystallite size data for the three cerias are given in Tables 1 and 2. Total hydrogen consumption values were well below the stoichiometric value for complete reduction, because the runs were discontinued at about 900°C, at which point reduction was still occurring.

It is clear from Fig. 1 that the first peaks are larger when surface area is higher, just as was reported by Yao and Yao (*1*). At 0.7 m^2/g the peak is barely visible to the eye, at about 600°C. The 650°C peak for 13 m^2/g is fairly well defined. The 27 m^2/g sample has two peaks below 650°C. The reason for this

TABLE 2

Cerium Dioxide

Sample	XRD Crystallite size (Å)	
	Measured	Calculated
I	633	12,000
II	331	647
III	132	312

is not known but is possibly related to the fact that Sample III is a mixture of two separately calcined materials, with surface areas of 25 and 29 m^2/g, respectively. It is the total area of these peaks which is of concern here, rather than their positions, since it is clearly much greater than that for Sample II. The relationship between area and hydrogen consumption in the first peak(s) for the three cerias is shown graphically in Fig. 2; the hydrogen consumption values are expressed in terms of the ratio of hydrogen atoms in the capping peak to total cerium atoms.

To relate these TPR data to crystallite sizes, or surface area, consider the ceria crystallites as cubes of n oxide ions on a side. Each crystallite will then contain n^3 oxide ions and $\frac{1}{2}n^3$ Ce ions. Since the ionic radius of the oxide ion is 1.40 Å, the crystallite size (a) will be

$$a = 2.80n \quad (\text{in Å}) \qquad (3)$$

The number of capping oxide ions in a crystallite is

$$O_c = n^3 - (n - 2)^3 = 6n^2 - 12n + 8 \qquad (4)$$

and

$$H_c = 2 \cdot O_c = \text{the number of H atoms to reduce half of the } O_c \text{ ions.} \qquad (5)$$

Therefore,

$$H_c/\text{Ce} = 2(6n^2 - 12n + 8)/n^3. \qquad (6)$$

The relationship between surface area and the TPR result in terms of H_c/Ce is obtained via a crystallite size calculation:

$$A = 60{,}000/da = \text{surface area} \quad (\text{in } m^2/g), \qquad (7)$$

where d = solid density = 7.13 g/ml for cerium dioxide; the factor of 60,000 includes the number of sides of a cube and the conversion factor from cm to Å.

For any given value of n, the H_c/Ce ratio

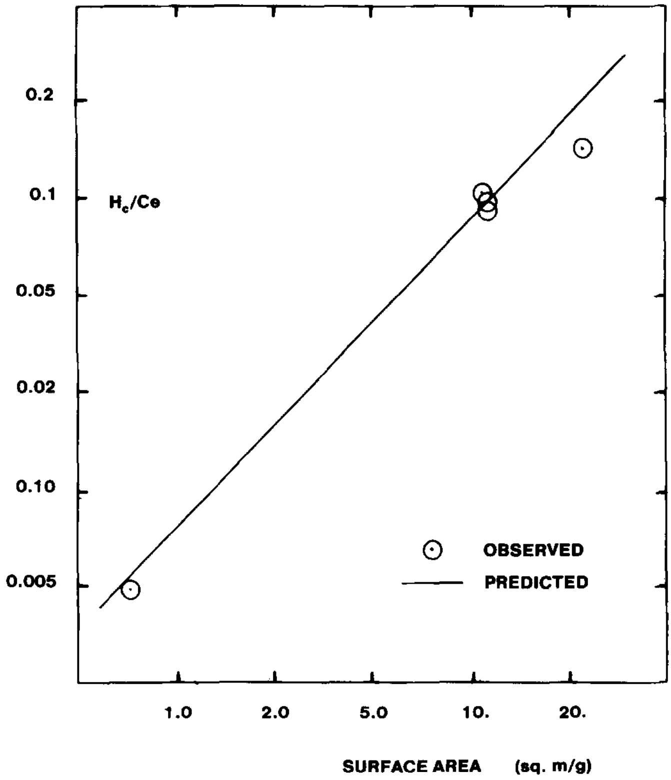

FIG. 2. Cerium dioxide; "capping" hydrogen vs surface area.

can be obtained from Eq. (6), and the surface area from Eq. (3) and (7). The predicted line in Fig. 2 and the predicted "capping" hydrogen consumptions for each sample shown in Table 1 were obtained in this fashion.

Clearly, there is good agreement between the values of H_c/Ce predicted from the surface areas of Samples I and II and their measured values, and less good agreement for Sample III. Regression of the log–log data of Fig. 2 led to a slope of 0.97, indicative of the expected linear relationship. The log–log plot shown here was used for clarity.

The XRD crystallite sizes of the three cerias are much smaller than those calculated from surface area by Eq. (7) (Table 2). The XRD line broadenings are clearly due to factors other than crystallite size. For this reason, we conclude that measurement of H_c/Ce is superior to XRD as a method for estimating the degree of subdivision of supported cerium dioxide. The same method should be applicable to other oxides which reduce in stages.

REFERENCES

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