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NOTE

Sintering of Pt/Al_2O_3 from Continuous Small-Angle X-Ray Scattering[1]

INTRODUCTION

Aggregation and redispersion phenomena significantly affect the behavior of supported-metal catalysts, and have consequently been the subject of many investigations, largely using static methods (see, for example, Refs. (*1–3*)). We report here the first of a series of small-angle X-ray scattering (SAXS) measurements on such catalysts, in this instance of Pt/Al_2O_3 in air, which permit us to follow changes in specific surfaces continuously as the sample is subjected to various treatments.

EXPERIMENTAL METHODS

Pt/Al_2O_3 catalysts with high Pt loadings (up to ~11 w/o) were chosen for these initial investigations.[2] Powder samples were formed into self-supporting rectangular platelets (27 × 6 × ~0.1–0.2 mm) in a stainless-steel mold to avoid some sample-handling problems, and in this form survived repeated temperature cycling from 20 to 700°C without cracking. The basic design of a sample cell similar to that used here was described previously (*5*). Some typical sample characteristics are given in Table 1.

Scattering measurements were made with a Kratky camera (*6*) modified to accommodate a one-dimensional position-sensitive detector (*7*). The camera was used in the "infinite slit" geometry, and slit-smeared intensity data were used directly (*8*). Instrumental background scattering, corrected for sample absorption, was found to be negligible in the angular range of the intensities used for subsequent calculations. Scattering curves between $h = 3 \times 10^{-3}$ Å^{-1} and $h = 0.13$ Å^{-1} were measured in 5 min, with a probable error of ~0.4% at the smallest and ~10% at the largest angles ($h = 4\pi\lambda^{-1} \sin\theta$; λ = X-ray wavelength, 1.54 Å for Ni-filtered Cu$K\alpha$ radiation; θ = half of scattering angle).

Sample temperatures were initially raised to 400°C within 1/2 h; the samples were then equilibrated for 10 min, and the scattering curve accumulated for 5 min. The temperature was subsequently raised through a series of steps to 500, 550, 600, 650, and 700°C (Fig. 1). As each temperature was reached, the samples were equilibrated for 10 min, then the scattering curves accumulated for 5 min before proceeding to the next temperature. At 700°C, the temperature was held constant for several hours, and a scattering curve was obtained once each hour. The samples were never cooled or removed from the sample cell during the heating program. Similar results were found with different equilibration and measurement intervals.

RESULTS AND DISCUSSION

Two quite different scattering models were used to analyze the intensity data: a model in which the catalyst components—metal, void, support—occupy randomly distributed polyhedral cells known as "Voronoi polyhedra" (*9*), and an alternative model which requires that the scattering of metal-free support be subtracted from the scattering of the catalyst (*4, 10*). For the Voronoi model, the theoretical correlation function $\gamma(r)$ (*9, 11*) is expressed in terms of parameters such as the average density of polyhedral nuclei, from which

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[2] Preparation and properties were described in Ref. (*4*). We are indebted to Dr. H.-G. Kim, then at Exxon Research and Engineering Laboratories, for some of the samples.

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TABLE 1

Characterization of A Typical Catalyst

Pt content	~11.3 w/o
Bulk density of catalyst by Hg displacement; d_B (g cm^{-3})	1.693
Skeletal density of catalyst by He displacement; d_S (g cm^{-3})	3.556

Volume fractions (1 = support, 2 = voids, 3 = metal)

$\phi_1^{(3)}$	0.467	$\phi_1^{(2)}$	0.467
$\phi_2^{(3)}$	0.524	$\phi_2^{(2)}$	0.533
$\phi_3^{(3)}$	0.0089		

Electron densities (mol $e \cdot$ cm^{-3})

n_1	1.578
n_2	0
n_3	8.576

Skeletal density of support (g cm^{-3})	3.217

the average interfacial areas per unit sample volume can be calculated (*9*). The theoretical slit-smeared intensity is found by Fourier-transforming $\gamma(r)$ appropriately, and the parameters in $\gamma(r)$ are determined by optimizing the fit of the theoretical intensity curve to the experimental scattering data. [Details of these calculations are given in Ref. (*9*).] For the "subtraction" model, calculations are based on the experimental quantity $\gamma'(0)$, the first derivative of the correlation function at the origin. The following relationships hold for slit-smeared quantities (*11–13*):

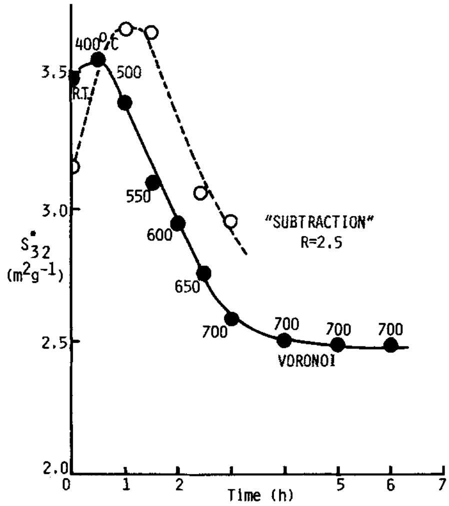

FIG. 1. Specific free metal surface S^{*}_{32} (m^2 per g catalyst), as function of time and temperature (°C), calculated from two scattering models.

$$\gamma'(0) = -\tilde{k}/\tilde{Q}, \tag{1}$$

where

$$\tilde{k} = \lim_{h\to\infty} h^3\tilde{I}(h), \tag{2}$$

and

$$\tilde{Q} = \int_0^\infty h\tilde{I}(h)dh. \tag{3}$$

Equation [2] is obeyed by our catalysts at sufficiently large scattering angles. $\tilde{Q}$ can be found numerically up to angles at which Eq. [2] is valid; at the smallest angles, an extrapolation to $h = 0$ is required, but the value of $\tilde{Q}$ is not sensitive to the details of this extrapolation. For larger angles, the integration can be done analytically using Eq. [2]. The quantity $\gamma'(0)$ is related to the surface-to-volume ratios S_{ij}/V (*12–14*). If $P_{ij}(r)$ is the probability that a line segment of length r lies with one end in phase i and the other in phase j, then

$$\left(\frac{dP_{ij}(r)}{dr}\right)_{r=0} = \frac{S_{ij}}{4V}. \tag{4}$$

Further (*14*),

$$\gamma(r) = 1 - \frac{\sum_{i>j} P_{ij}(r)(n_i - n_j)^2}{\overline{n^2} - \bar{n}^2}, \qquad (5)$$

and therefore

$$\gamma'(0) = -\frac{1}{4V}\frac{\sum_{i>j} S_{ij}(n_i - n_j)^2}{\overline{n^2} - \bar{n}^2}. \qquad (6)$$

$\overline{n^2}$ is the mean-square electron density of the sample, $\bar{n}$ ($= \Sigma_i \phi_i n_i$) the average electron density, ϕ_i are the volume fractions, and n_i the electron densities of the phases. We assume that the samples are spatially isotropic, that the phase boundaries are sharp and smooth, and that no appreciable changes occur in ϕ_i and n_i when the samples are heated. The ϕ_i are found from skeletal and bulk density measurements, n_i from the mass densities of the phases. For a three-phase system, there are three independent surfaces S_{21}, S_{31}, S_{32} (where the subscript 1 refers to support, 2 to void, 3 to metal). Two relationships among the P_{ij} are therefore required in addition to $\gamma'(0)$, and these are furnished by the model. For three-phase catalyst [superscript (3)] and two-phase support [superscript (2)], taking $n_2 \approx 0$, support structure the same in support and catalyst, and some of the void phase of the support filled by metal, one obtains

$$\frac{S_{32}^{(3)}}{4V}(\text{Å}^{-1}) = \frac{[\overline{\eta^2}\gamma'(0)]^{(2)} - [\overline{\eta^2}\gamma'(0)]^{(3)}}{[(1 + R)n_3^2 - 2n_1 n_3]R^{-1}}, \qquad (7)$$

where R is $S_{32}^{(3)}/_{31}^{(3)}$, the ratio of free to covered metal surface (*10*). $\overline{\eta^2} = \overline{n^2} - \bar{n}^2$, $\gamma'(0)$ and the n_i are known, and $S_{32}^{(3)}/V$ is consequently found in terms of R, which is ~ 1 for rafts, 2 for hemispheres, 3 for tetrahedra, etc. The surfaces in Fig. 1 are calculated for $R = 2.5$. Surfaces have been calculated using the electron density of metallic platinum, which we consider appropriate in view of the low dispersity and substantial particle size (*2, 3, 10, 15*). The presence of surface oxides would not materially alter our analysis. The specific surface, S_{ij}^* (m^2 g^{-1}), is found from the bulk density d_B (g cm^{-3}):

$$S_{ij}^* = \frac{S_{ij}}{V} \cdot \frac{10^4}{d_B}. \qquad (8)$$

From Fig. 1, it is evident that both models indicate an initial redispersion (*16–19*) at 400–500°C and that the surface then decreases as the temperature is raised further. This is in good agreement with other, static, measurements (*20*), which show, from H_2-chemisorption data on Pt/γ-Al_2O_3 samples treated in O_2 for 2 h at various temperatures and then cooled, that redispersion occurred at treatment temperatures below about 550°C, and sintering at 600°C and above. The response of the catalyst to temperature changes appears to be quite rapid, and most of the sintering has already occurred by the time the 700°C soaking temperature is reached. The sintered samples, after cooling to room temperature, showed lower $\gamma'(0)$-values than those observed before sintering. Clearly, the SAXS method is capable of following changes in surface areas accurately, nondestructively and continuously *in situ,* for a wide variety of temperature, pressure, and ambient atmosphere conditions. Further such experiments are currently in progress.

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