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Characteristics of Particle Size Distribution Functions of a Supported Metal Catalyst during Sintering

INTRODUCTION

It has been recognized for years that to arrive at an identification of the mechanism of thermal sintering of catalysts one requires detailed characterization of the metal particle size distribution (PSD) function during sintering. However, obtaining the necessary data has only recently been made possible with the development of a reliable X-ray method which is capable of determining the PSD. In earlier papers, the X-ray analysis technique (*1*) and the results of an extensive sintering study of a nickel catalyst supported on silica were reported (*2*). The PSD functions reported in this earlier paper were subjected to an analysis suggested by Granqvist and Buhrman (*3*) in an attempt to provide additional support for the proposed sintering mechanisms. The purpose of this paper is to report the analysis performed on the existing PSDs and to show that the results provide further evidence that sintering at temperatures of 700°C and below takes place by particle migrations and that during 800°C sintering the atomic migration mechanism becomes operative. The analyses reported here are mainly concerned with fitting the existing PSDs to log-normal distribution functions (LNDF), and observing the behavior of the standard deviations of the PSD functions related to sintering time, sintering temperature, and the geometric mean average particle size.

EXPERIMENTAL AND ANALYSIS

The catalyst C-150-10-1 supplied by United Catalysts, Inc., Louisville, Ky., is a nickel catalyst supported on silica produced by a coprecipitation process (*4*). The catalyst had a chemistry of 51.7% Ni, 2.94% C, and 0.06% S, a specific area of 211 m^2/g and a density of 1.05 g/cm^3. The nickel oxide, which existed in the as-produced coprecipitated catalyst (*4*), was reduced 3 hr at 500°C under hydrogen. The as-reduced material was sintered under nitrogen and hydrogen atmospheres at temperatures between 500 to 800°C for times up to 100 hr. Complete experimental details were presented in Ref. (*2*).

A single-profile X-ray analysis (*1*) was performed on the (200) diffraction profile from nickel. This analysis technique gives, in addition to the normal diffraction structural parameters, the particle size distribution function, which in the case of this particular catalyst is the distribution function of nickel particles residing on the silica support.

The PSD functions were fitted to LNDF as proposed by Granqvist and Buhrman (*3*). They presented the LNDF as (note the D term in the denominator was missing in their manuscript):

$$P(D) = [1/((2\pi)^{1/2} D \ln \sigma)] \exp - [(\ln D - \ln Dg)/((2)^{1/2} \ln \sigma)]^2, \quad (1)$$

where σ, the standard deviation, and D_g, the geometric mean particle size, are defined by

$$\ln Dg = \Sigma_i n_i \ln D_i (\Sigma_i n_i)^{-1}$$

and

$$\ln \sigma = (\Sigma_i n_i (\ln D_i - \ln Dg)^2 (\Sigma_i n_i)^{-1})^{1/2}. \quad (2)$$

Granqvist and Buhrman (*3*) presented an analysis of a number (approximately 15) of

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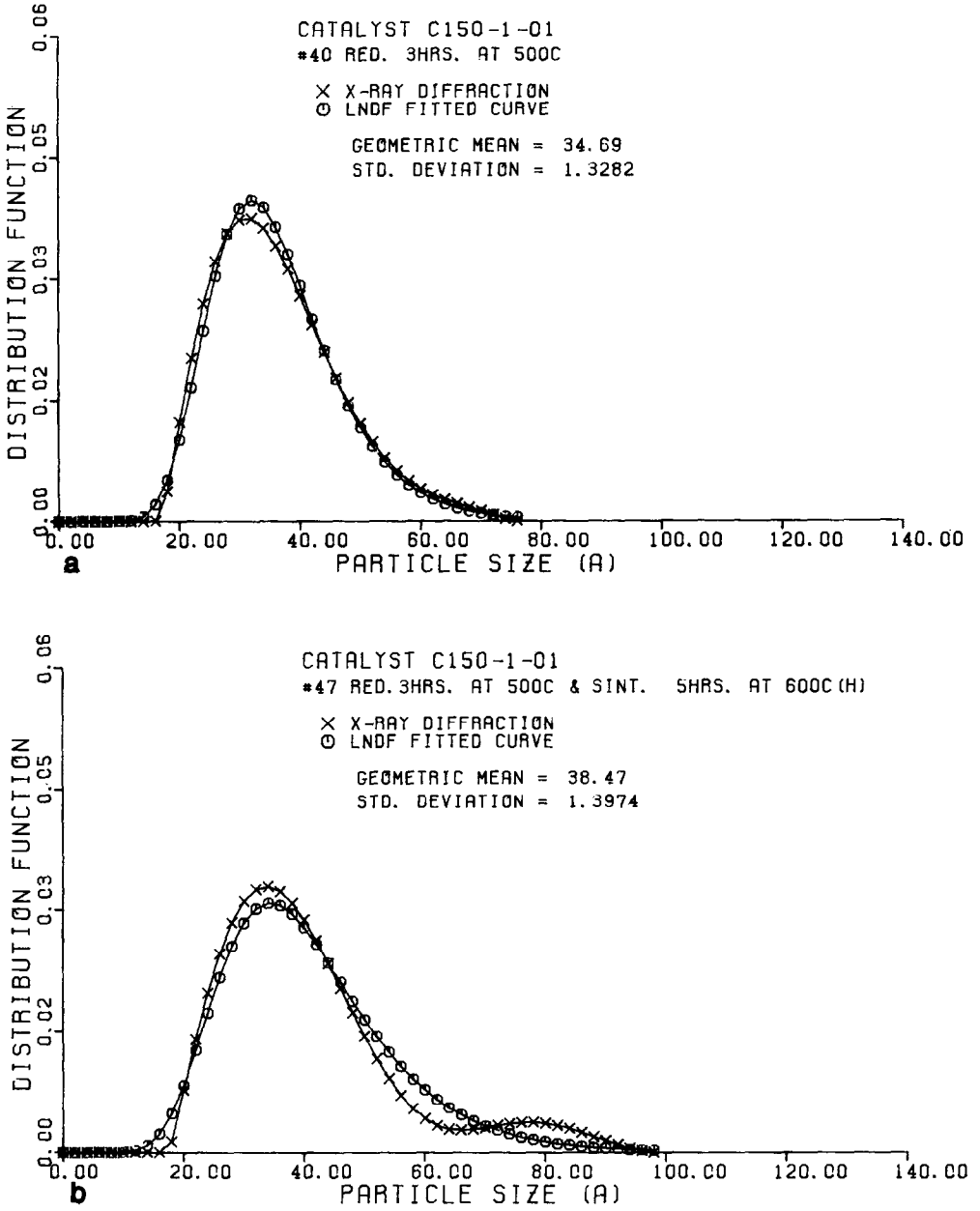

FIG. 1. Typical plots of the log-normal distribution function (LNDF) fitting to the particle size distribution function determined from X-ray diffraction on (a) the as-reduced catalyst, (b) after sintering under hydrogen atmosphere, and (c) after sintering under nitrogen atmosphere.

PSD functions from a number of literature sources. Their results showed that the PSDs fit LNDFs and the standard deviations of the distributions were between 1.20 and 1.44. They further interpreted these results to indicate that when sintering takes place by the operation of a particle migration mechanism the distribution of metallic particles is log normal in character. In response to the latter hypothesis, Wanke

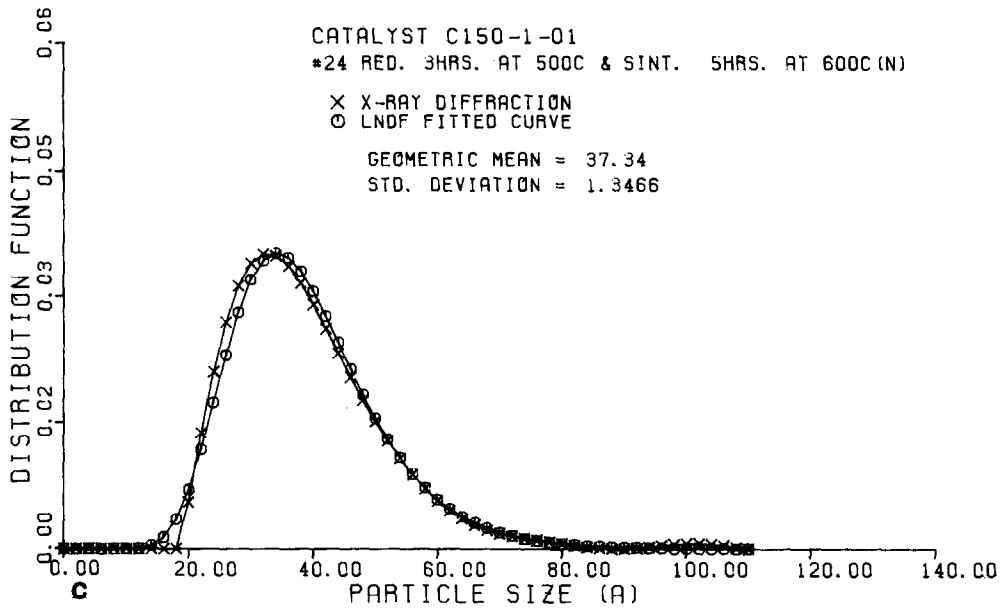

FIG. 1—*Continued.*

(*5*) argued that particles formed during sintering by an atomic migration mechanism could also follow a LNDF if the initial PSD is log-normal.

The PSD functions determined in the investigation of the sintering behavior of catalyst C-150-1-01 were fitted to LNDFs by calculating the standard deviation and geometric mean particle size from the X-ray-determined PSD functions (*2*). All of the PSD functions were found to fit LNDFs very well. Typical results of the fits obtained are shown in Fig. 1 for the catalyst in the as-reduced condition and after sintering the catalyst in both the hydrogen and nitrogen atmospheres. In a few cases where the PSD functions displayed a slight bimodal character the LNDF fit was still extremely good. For the purpose of this work the PSD functions are considered to be unimodal.

A summary of the values of the standard deviation geometric mean particle sizes, and the χ^2 fitting parameters for all the PSD functions are given in Table 1. A χ^2 value of 1089 indicates a 95% reliability of fit; clearly all of the fits are considerably better than this. The values of the standard deviation associated with the PSDs obtained from the as-reduced catalysts and after sintering at temperatures of 700°C and below are between 1.27 and 1.51, very close to the range reported by Granqvist and Buhrman (*3*). Furthermore, there are no systematic variations in the values of the standard deviation at any particular sintering temperature. However, values of the standard deviation increase as the particle size increases and the range of standard deviation value is small (0.06 to 0.11) at all sintering temperatures, except 800°C, where the range is 0.22 for sintering in nitrogen and 0.49 for sintering in hydrogen.

Sintering at 800°C produces an increase in the values of the standard deviation and the values increase with increasing sintering time. Furthermore, values of the standard deviation as high as 1.97 were obtained, which is significantly out of the range 1.20–1.44 observed by Granqvist and Buhrman. Other data, including the order of sintering, reported on this catalyst also show significant changes at 800°C (*2*), which when considered collectively indicate that there is a change in the sintering mechanism at this temperature compared to lower sintering temperature. The varia-

TABLE 1

The Values of Geometric Mean, Standard Deviation, and χ^2 Test Obtained from a LNDF Fitting of the PSD

Run number	Sintering			LNDF		χ^2 test value
	Temp. (°C)	Time (hr)	Atm.	Geometric mean	Standard deviation	
17	—	—	—	35.1	1.31	11.8
25	—	—	—	33.1	1.29	6.9
32	—	—	—	34.2	1.37	10.4
40	—	—	—	34.7	1.33	7.6
18	500	5	N	35.8	1.36	19.1
19	500	10	N	34.2	1.32	17.6
35	500	20	N	38.4	1.35	22.6
20	500	50	N	35.5	1.30	18.4
24	600	5	N	37.3	1.35	43.5
26	600	10	N	37.0	1.39	13.3
27	600	20	N	36.4	1.35	14.2
21	600	50	N	39.3	1.36	16.9
23	600	100	N	39.1	1.41	30.8
77	700	5	N	41.9	1.45	13.3
70	700	10	N	41.1	1.48	24.0
31	700	20	N	53.6	1.42	14.2
33	700	50	N	54.1	1.44	28.3
34	700	100	N	51.3	1.43	39.3
72	800	1	N	41.3	1.55	6.1
73	800	5	N	55.8	1.55	12.2
74	800	10	N	52.5	1.65	5.6
75	800	20	N	62.6	1.58	4.8
76	800	50	N	59.2	1.77	11.7
41	500	5	H	34.1	1.27	24.5
42	500	10	H	36.0	1.37	8.5
43	500	15	H	35.3	1.35	15.7
44	500	20	H	37.6	1.38	25.5
45	500	50	H	35.5	1.31	11.1
47	600	5	H	38.5	1.40	50.1
48	600	10	H	37.7	1.41	24.5
49	600	15	H	33.9	1.37	42.7
50	600	20	H	39.3	1.37	36.5
51	600	50	H	40.3	1.43	139.6
53	700	5	H	44.8	1.45	16.3
54	700	10	H	45.0	1.47	22.0
55	700	15	H	47.6	1.47	17.3
56	700	20	H	45.2	1.48	8.4
57	700	50	H	49.8	1.51	23.8
66	800	1	H	60.4	1.48	3.5
59	800	5	H	67.6	1.61	48.7
60	800	10	H	64.1	1.74	48.4
61	800	15	H	66.0	1.72	8.0
62	800	20	H	86.8	1.97	78.0

tion in the values of the standard deviation is an additional indication of this change in the sintering mechanism.

DISCUSSION

The results presented clearly indicate that all of the PSD functions are log normal in character. Although Granqvist and Buhrman interpreted this as meaning that the operative sintering mechanism was particle migration (*3*), they were only dealing with systems in which the PSDs had standard deviations between 1.20 and 1.44. The data generated here suggest that the value and the behavior of the standard deviation of the PSD functions, at a particular sintering temperature, aid in identifying the operating mechanism. At all sintering temperatures below 800°C the standard deviation is constant with sintering time, within experimental variations. The experimental variation is taken to be the spread in data observed in the four determinations made on the as-reduced catalyst (see Table 1). Therefore the distribution functions are constant and simply shift to larger sizes with increasing sintering time at all sintering temperatures below 800°C. However, during 800°C sintering the distribution function broadens with sintering time, a behavior very different from that for the lower-temperature sintering data and consistent with the operation of a complex sintering mechanism in which time-varying interactions with the pore structure of the support are occurring. This is thought to be an atomic rather than a particle migration process and the interaction with the support starts as the particles fill the pore section in which it resides. A second possibility for the explanation of the behavior observed at 800°C is that the nickel metal is reacting chemically with the support to form $NiSO_3$. As this reaction occurs, at the metal–support interface, the particle migration process would be suppressed and sintering would continue by an atomic migration mechanism. If either of these hypotheses is confirmed, as more PSD data on sintered catalysts become available, the standard deviation of a particle size distribution function will be a useful parameter in identifying the operative sintering mechanism.

If a relationship could be shown to exist between the two parameters in the LNDF, the LNDF would reduce to a one-parameter function. A plot of the geometric mean versus the standard deviation obtained from the PSD functions obtained during sintering of the catalyst investigated tends to strongly indicate that a linear relationship exists between these two parameters; see Fig. 2. Once this relationship is established, it will be possible to determine the geometric mean particle size using a routine experimental method, such as gas absorption, obtain the corresponding standard deviation from Fig. 2, and generate the particle size distribution function using Eq. (1).

The data in Fig. 2 can be thought to be a characteristic curve for a catalyst and once obtained would make it possible to construct particle size distribution functions, a relatively easy task.

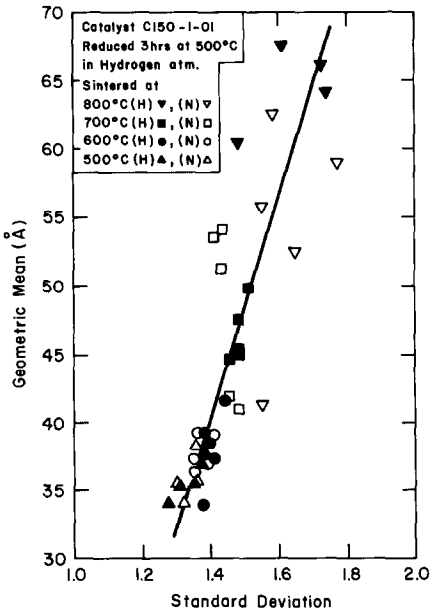

FIG. 2. Plot of the geometric mean vs the standard deviation determined from the log-normal distribution fitting of the PSDs for catalyst C150-1-01.

CONCLUSIONS

(1) Nickel particles on a silica support follow a LNDF both in the as-reduced condition and after sintering at temperatures up to 800°C.

(2) The values of the standard deviation of the particle size distribution functions increase with sintering temperature. The time-dependent increase of the standard deviation observed at the highest sintering temperature is a possible indicator of a change in sintering mechanism.

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