

INFLUENCE OF PREPARATIONAL VARIABLES
ON THE CRYSTALLITE SIZE DISTRIBUTION
OF NICKEL CATALYSTS

A Thesis
Presented to
the Faculty of the Department of Chemical Engineering
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemical Engineering

by
Regis J. Dubus
July, 1977

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ABSTRACT

Nickel catalysts were prepared by precipitation--deposition of nickel in an aqueous solution containing the suspended silica support. The solution was well stirred and maintained at 90° C. At this temperature, urea added to the solution slowly decomposes to release hydroxyl ions throughout the aqueous suspension. The increase of pH causes the nickel ions to precipitate uniformly and deposit onto the silica carrier. After washing and drying the nickel content of the catalyst was determined chemically.

The crystallite size distribution (CSD) of the catalysts prepared by this method was determined from low-field magnetic measurements.

The influence of some preparational variables on the CSD of the catalysts was investigated. They included the precipitation time, composition of the solution, nature of the support, initial pH, reduction time, temperature and flow rate and effect of calcination. The effect of adsorbed hydrogen and passivation by oxygen on the magnetization of the catalysts was also studied on selected samples.

The results indicate that the preparation method is particularly suitable for control of the CSD of the catalysts. Uniformly dispersed catalysts with very small crystallites can be prepared in a reproducible manner.

Variables affecting the CSD to a great extent are the total nickel content (governed by composition of the solution and precipitation time), the nature of the support and the reduction temperature.

Longer reduction times and higher hydrogen flow-rates result in increased amounts of reduced nickel without increasing the crystallite sizes.

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1. INTRODUCTION

Supported catalysts are widely used because of their high specific activity. This activity results from the dispersion of active material as very small particles onto the support during the preparation process, giving a high surface area for adsorption-reaction-desorption. However, the complexity of the surface phenomena and chemistry during a classical preparation operation (impregnation, precipitation, co-precipitation) is such that the size of the active particles cannot be effectively controlled. As a result, a typical supported catalyst will display a crystallite size distribution around an average value. The discussion presented in the next paragraph will emphasize the importance of this distribution regarding the activity, selectivity, adsorption properties and sintering properties.

The objective of this work is to investigate a method of preparation whose variables are controllable and to study the effect of these variables on the crystallite size distribution. The parameters of pretreatment (calcination, temperature of reduction, time of reduction, hydrogen flow-rate, stabilization) influence the final product and are also studied.

A method to determine the crystallite size distribution of supported nickel catalysts from magnetic measurements has been developed in this laboratory⁽¹⁾. The method presented in detail in Section 3 is limited to very small crystallites of ferromagnetic material so that nickel is a favored choice. J.A. Van Dillen and

co-workers⁽²⁾ recently proposed a method to prepare nickel on silica catalysts by homogeneous and slow precipitation-deposition of nickel hydroxyl in an aqueous suspension of silica. Although they did not report any data on particle sizes, the method promises to be suitable for our purpose because most of the preparation variables are controllable due to the homogeneous nature of the process. The slow decomposition of urea in water above 70°C is used as a controlled source of hydroxyl ions. In the presence of nickel ions and silica, these hydroxyl ions combine with nickel to precipitate slowly and homogeneously throughout the suspension and deposit on the silica in a uniform manner.

It can be expected that catalysts prepared in such a way would exhibit a uniform dispersion of very small nickel particles.

A series of catalysts was prepared by this method varying the time of precipitation, the composition of the solution and the nature of the support. The effect of pH on the initiation of the precipitation was checked on one batch. All other parameters were kept constant (temperature of the solution, stirring, washing and drying conditions).

The catalysts were reduced at 400°C in H₂ (flow-rate 30 cc/mm) for 15 hours. The effect of flow-rate, reduction time and reduction temperature was studied in a few selected samples. The effect of calcination at 350°C and 450°C in air prior to reduction was also checked. Finally in one case, the effect of adsorbed hydrogen and oxygen on the magnetization was determined.

The total nickel content was determined chemically in the silica supported catalysts. The reduced nickel content was deduced from

the saturation magnetization of the catalyst. The metallic surface area was calculated from the crystallite size distribution assuming a spherical shape.

2. CRYSTALLITE SIZE EFFECTS

Crystallite size in a supported catalyst needs to be known if one is to study the catalyst activity and selectivity, adsorptive properties and the sintering mechanisms.

21. Effect of Crystallite Size on Activity and Selectivity

Two catalysts having the same surface area but a different particle size distribution may not have the same specific activity, and this activity will depend on the shape of the distribution.⁽³⁾ Therefore, it is important to control the sizes of particles during preparation and to measure their distribution whenever one reaction involved is demanding. A demanding reaction is one whose intrinsic activity depends on the structure of the catalysts (nature of the support, metal dispersion and concentration, crystallite shape and defects). Examples of demanding reactions are the hydrogenation of benzene by nickel on silica catalysts⁽⁴⁾ and ethane hydrogenolysis by nickel on silica-alumina catalysts.⁽⁵⁾ On the other hand, the hydrogenation of benzene, cyclohexene and cyclopropane by platinum on alumina are facile reactions:⁽⁶⁾ the activity per exposed metal atom is independent of crystallite size.

In processes like catalytic reforming where many reactions occur simultaneously, crystallite size effect on activity can influence the selectivity if one or several reactions are demanding.

For example, during reforming of n-heptane by platinum on alumina catalyst, the activity of hydrocracking and dehydrocyclization decreases

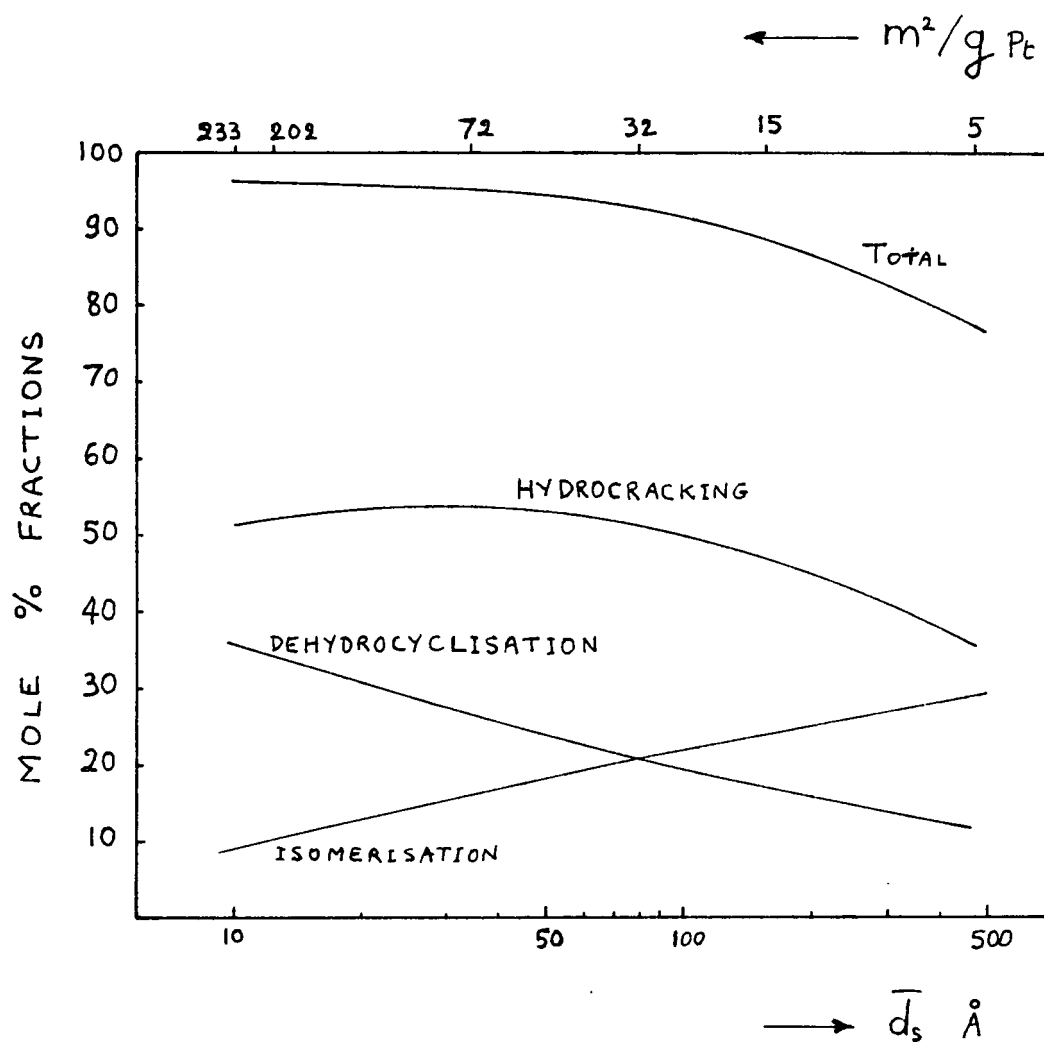


FIGURE 21
 Product Distribution for n-heptane Reforming
 (Ref. 7)

with increasing particle size whereas isomerization activity appears to increase.⁽⁷⁾ From Fig. 21, it is obvious that an increase in platinum size of the catalyst results in lower octane number since the aromatics formed by dehydrocyclization contribute considerably more to the octane number than the isomerized paraffins.

In this case, a highly selective platinum reforming catalyst must have platinum crystallites in the range 10-20 Å and greatest possible resistance to sintering. It illustrates the need for control of the particle size during catalyst preparation and for understanding the sintering mechanisms under process conditions.

22. Sintering of Supported Catalysts

During use or regeneration supported catalysts are often exposed to high temperatures and gradually lose activity even if poisoning or fouling does not occur. Heat treatment of the catalyst causes the metallic particles to grow and the active surface area to decrease accordingly- This undesirable effect is referred to as sintering and has been studied extensively.⁽⁸⁾

Two models have been proposed to describe the mechanisms of particle growth. In the "particle migration model" metallic particles are believed to migrate along the support until they collide and coalesce with each other, forming bigger crystallites. A comprehensive treatment of this model has been put forward by Ruckenstein and Pulvermacher.^(9,10,11,12)

The second model, proposed by Flynn and Wanke^(13,14,15) considers the sintering to occur by dissociation of atomic species from the metal crystallites. These atomic species migrate over the support surface and collide with the stationary metal crystallites: it is called the interparticle transport model. In both models, the driving force for crystallite growth is the reduction of surface energy. A summary of the assumptions used in the two models along with their predictions is given in Appendix 1. However, as pointed out by Wynblatt and Ahn⁽¹⁶⁾ both mechanisms can account for a wide variety of phenomena and no conclusive statement has been made possible up to now. The only way to identify the sintering mechanisms is the evolution of the particle size distribution with time, since average size measurement only is not a conclusive piece of information.^(12,15,16) But Wynblatt and Ahn⁽¹⁶⁾ clearly showed that the evolution of the distributions predicted by the two models can be very similar, making the identification difficult. It appears that only a uniformly distributed catalyst can be used for unambiguous conclusions. Flynn and Wanke⁽¹⁵⁾ showed that such a catalyst is predicted not to sinter at all or very slowly in the atomic interparticle transport model, while it is predicted to sinter readily in the particle migration model. Achieving catalysts with the narrowest possible CSD should therefore allow conclusive experimental study of the sintering mechanisms.

23. Energetics of Adsorption

It is well established that the mechanism of a heterogeneous catalytic reaction depends on the nature and characteristics of the adsorption of at least one reactant on the catalyst. The energetics of this adsorption is often complex mainly because many catalysts have energetically non-uniform surfaces. Species at the corners or edges of the crystallite may have adsorption energies very different from the species located on a plane. When a reaction occurs only a fraction of sites may have the activation energy required for adsorption of the reactant(s) and desorption of the product(s).⁽¹⁷⁾ The proportion of sites of a given kind depends in turn on the crystallite size.

Thus it is expected that the activity of a catalyst will vary with crystallite size in some reactions, as a result of changes in the energetics of adsorption. A study of the influence of crystallite size on the energetics of adsorption is therefore a key factor to understand the mechanisms of demanding and facile reactions. In this context, the need for controlling the particle size distribution appears clearly.

3. MEASUREMENT AND CALCULATION OF THE CRYSTALLITE SIZE DISTRIBUTION

A method to calculate crystallite size distributions from magnetic measurements has been developed in this laboratory.⁽¹⁾ The method applies to small ferromagnetic particles (less than 200 Å diameter) and utilizes the so-called superparamagnetic behaviour of these particles. The technique therefore applies to finely dispersed nickel catalysts.

3.1. Computation Technique

The magnetization M of superparamagnetic particles placed in a magnetic field of strength H is given by the Langevin equation:

$$M = I_s v L \left(\frac{I_s H v}{k T} \right)$$

where I_s is the spontaneous magnetization, v the volume of the particle, k the Boltzmann constant and T the temperature.

The Langevin function L is:

$$L(x) = \coth x - \frac{1}{x}$$

$L(x) \approx x/3$ when x small

$L(x) \approx 1 - \frac{1}{x}$ when x very large

When H tends to ∞ , the quantity

$$M_{\infty} = I_s v$$

is the saturation magnetization which does not depend on particle size.⁽²²⁾ The ratio $\sigma = \frac{M}{M_\infty}$ is the relative magnetization and is given by:

$$\sigma = \frac{M}{M_\infty} = L\left(\frac{I_s H v}{k T}\right) \quad (1)$$

At a given temperature, the relative magnetization σ will depend on field strength applied and on the volume of the particle.

If we have a particle size distribution with density function $f(v)$, the equation 1 generalizes to:

$$\frac{M}{M_\infty} = \int_0^\infty f(v) L(v, H) dv$$

For convenience, let us assume a spherical shape: the particle volume becomes $v = \frac{4}{3}\pi r^3$, r being the radius. Now

$$\frac{M}{M_\infty} = \int g(r) L(r, H) dr \quad (2)$$

Discretizing equation (2) gives:

$$\frac{M}{M_\infty}(H) = \sum_{i=1}^n g(r_i) L(r_i, H) \quad (3)$$

where i is a selected interval over r , $g(r_i)$ and $L(r_i, H)$ are the average values of $g(r)$ and $L(r, H)$ on each interval i .

For n different values of the field, equation (3) produces a system of n equations:

$$\begin{aligned}
 \left(\frac{M}{M_\infty}\right)_{H_1} &= g(r_1) L(r_1, H_1) + \dots + g(r_n) L(r_n, H_1) \\
 (S3) \quad \left(\frac{M}{M_\infty}\right)_{H_2} &= g(r_1) L(r_1, H_2) + \dots + g(r_n) L(r_n, H_2) \\
 &\vdots \\
 \left(\frac{M}{M_\infty}\right)_{H_n} &= g(r_1) L(r_1, H_n) + \dots + g(r_n) L(r_n, H_n)
 \end{aligned}$$

The quantities $L(r_i, H_i)$ are calculated readily and $\left(\frac{M}{M_\infty}\right)$ at a field H_i is determined experimentally (see Section 33).

The system of n linear equations has n unknowns which are the distribution coefficients $g(r_i)$. It is solved by a computational scheme described in detail earlier.⁽¹⁾

A set of initial values for the $g(r)$'s need to be guessed to start the iteration.

In order to get a set of initial values as close as possible to the result, a Log-normal distribution is used by adjusting two parameters: r_0 , the average radius, and s , the variance of the distribution. This adjustment of the initial guess distribution is done by using experimental data at low field and high field.

At low field,

$$L(r, H_{LF}) \approx \frac{4\pi I_s H_{LF}}{g k T} r^3 \quad (4)$$

Then equation (2) becomes:

$$\left(\frac{M}{M_{\infty}}\right)_{LF} = \frac{4\pi I_s H_{LF}}{g \downarrow k T} \int_0^{\infty} g(r) r^3 dr \quad (5)$$

Equation (5) allows to determine $\overline{r^3} = \int_0^{\infty} g(r) r^3 dr$ (third moment of the distribution) from a measurement of the relative magnetization at a low field value H_{LF} .

At high field,

$$L(r, H_{HF}) \approx 1 - \frac{3kT}{4\pi I_s H_{HF} r^3} \quad (6)$$

and equation (2) gives

$$\left(\frac{M}{M_{\infty}}\right)_{HF} = \int_0^{\infty} g(r) \left[1 - \frac{3kT}{4\pi I_s H_{HF} r^3}\right] dr \quad 4\pi$$

which rewrites as

$$\left(\frac{M}{M_{\infty}}\right)_{HF} = 1 - \frac{3kT}{4\pi I_s H_F} \int_0^{\infty} \frac{1}{r^3} g(r) dr \quad (7)$$

From equation (7)

$$\overline{r^{-3}} = \int_0^{\infty} \frac{1}{r^3} g(r) dr$$

can be determined if one has a high field measurement. Thus, the moments of order 3 and -3 of the distribution can be estimated.

Now, for a log-normal distribution with parameters r_0 and S :

$$f(r) = \frac{1}{\sqrt{2\pi} r \ln S} \exp\left[-\left(\frac{\ln r - \ln r_0}{\sqrt{2} \ln S}\right)^2\right]$$

the n^{th} moment is

$$\overline{r^n} = \int_0^\infty r^n f(r) dr = \exp\left[n \ln r_0 + \frac{n^2}{2} \ln S\right]$$

Therefore, knowing $\overline{r^3}$ and $\overline{r^{-3}}$ allows to calculate r_0 and S . The resulting log-normal distribution is taken as the initial guess for the calculation of the crystallite size distribution. The data and units needed for calculations are:

$$k = 1.38 \times 10^{-16} \text{ erg molecule}^{-1} \text{ K}^{-1}$$

$$I_s = 485 \text{ gauss}$$

T , temperature in K

H , field strength in gauss

$\frac{M}{M_\infty}$, dimensionless relative magnetization

r , particle radius in cm

32. Model Calculations

The computation technique presented briefly has been successfully tested on a number of model distributions in the past.⁽¹⁾ The test consists of two steps:

1. The magnetization curve is calculated for an assumed distribution.
2. The result of Step 1 is used as data to recalculate the CSD coefficients.

The assumed and recalculated distributions will be identical in the ideal case.

P. Desai⁽¹⁾ found the agreement to be excellent for log-normal assumed distributions. For less regularly shapes or bimodal type distributions, the agreement is poorer but still much acceptable. In the present work where low field data only were available and where many of the catalysts displayed very small crystallites, it was necessary to check the validity of the method in situations close to reality, i.e., at fields from 0 to 8 Kgauss and for narrow CSD's in the range 0-50 Å.

Model calculations are given in Appendix C.

For particles in the range 2.5 to 22.5 Å with most of the particles at 12.5-15.0 Å, the calculated distribution is not in good agreement with the assumed one (Fig. C1). This is for the case where the magnetization values are computed at low fields (0 to 8 Kgauss). However, the maximum of the distribution is correct and the range of sizes (2.5 to 22.5 Å) is acceptable. Keeping the same distribution

of sizes but in the range 15 to 37.5 Å and 27.5 to 50 Å, the calculated distribution is closer to the assumed one (Fig. C2 and C3). Other models show the same trend (Fig. C4, C4, C6): At low fields values, small particles in the range 0-10 Å are not properly accounted for. However, if the calculation is performed at high field values (0 to 80 Kgauss) on an assumed distribution containing very small particles, then the agreement becomes good (Fig. C7). The reason for this is that at low field values, the magnetization curve M/M_∞ vs. H is almost a straight line for small particles (Fig. 32). In that case, the Langevin function $L(r,H)$ becomes almost proportional to H . It means in turn that the system of n equations (S3) approaches a situation where the n linear equations are "almost linearly dependent." From a numerical point of view, the determinant of the system will approach zero and there will be many solutions within the accuracy of the computation.

To see if the initial guess distribution used to start the iterative scheme was important, a flat initial distribution was also used in most cases. This flat distribution has twenty coefficients equal to 0.05. The difference with the log-normal distribution is not significant. The calculated surface areas in both cases (flat and log-normal initial distribution) are both very close to the surface area of the assumed distribution.

In conclusions, this discussion emphasizes the need for high field data (or alternatively very low temperature measurements) if one wants reliable quantitative information on very small crystallites.

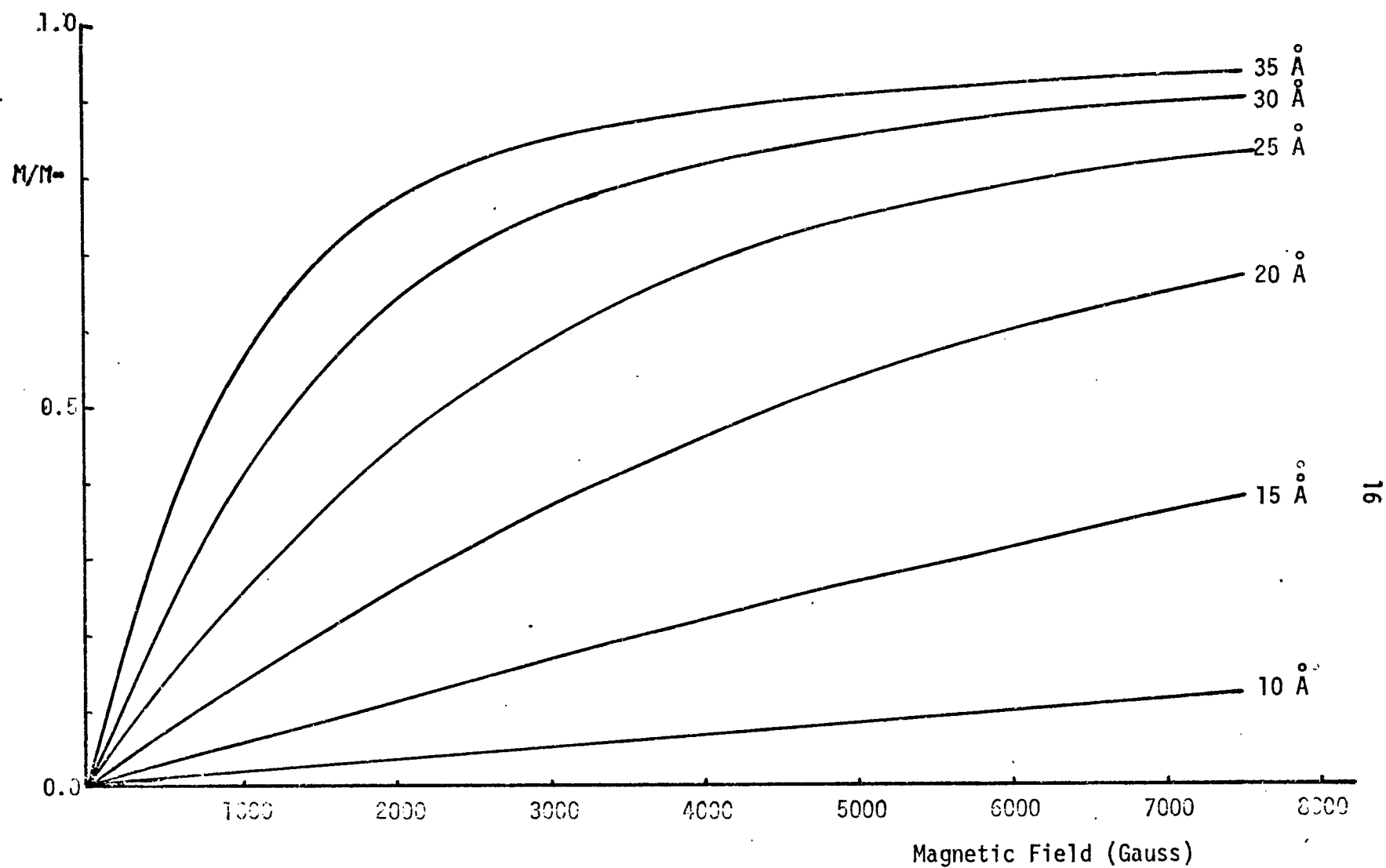


Fig. 32 Relative Magnetization Curves for Unisized CSD

In such conditions, the realtive magnetization curve will display a pronounced curvature, avoiding the loss of information encountered when low field and room temperature measurements are used. Unfortunately, temperatures down to a few degrees Kelvin or high fields up to 80 Kgauss require time consuming and expensive experimental procedures.

The low field data obtained at room temperature throughout this work allowed fast and convenient measurements on many samples but with some sacrifice in quantitative information in the case of small particles (less than $15 \text{ \AA}$ radius).

33. Experimental Measurement of Magnetization

The experimental apparatus is a rotating-coil magnetometer described in detail earlier.⁽¹⁾

Fig. 33 represents the main features of the system. A few modifications have been made to increase signal stability and sensitivity. These are the following:

1. The number of turns on each induction coil was increased to 500 (compared to 390 previously).
2. On the original system, there was one carbon brush making contact with the rotating brass ring. The modified system has now three carbon brushes per ring separated by an angle of 120° . It results in better mechanical support of the rotating shaft and less noisy electrical contact.

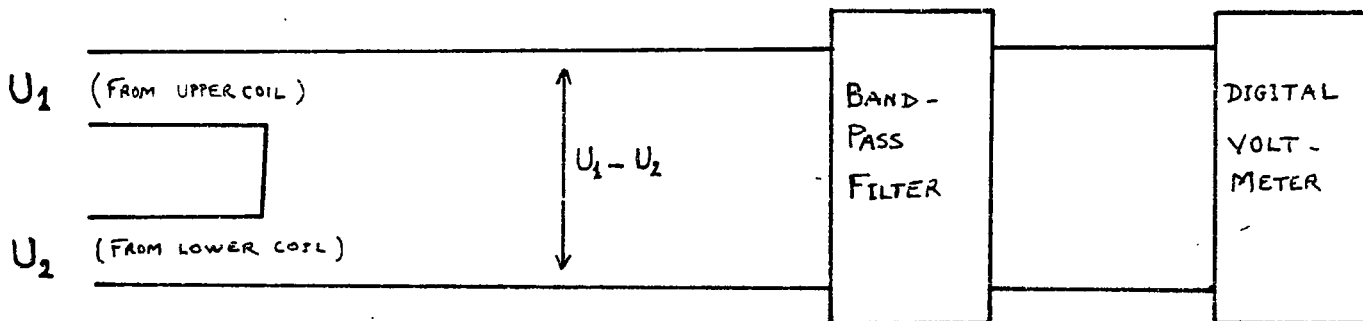
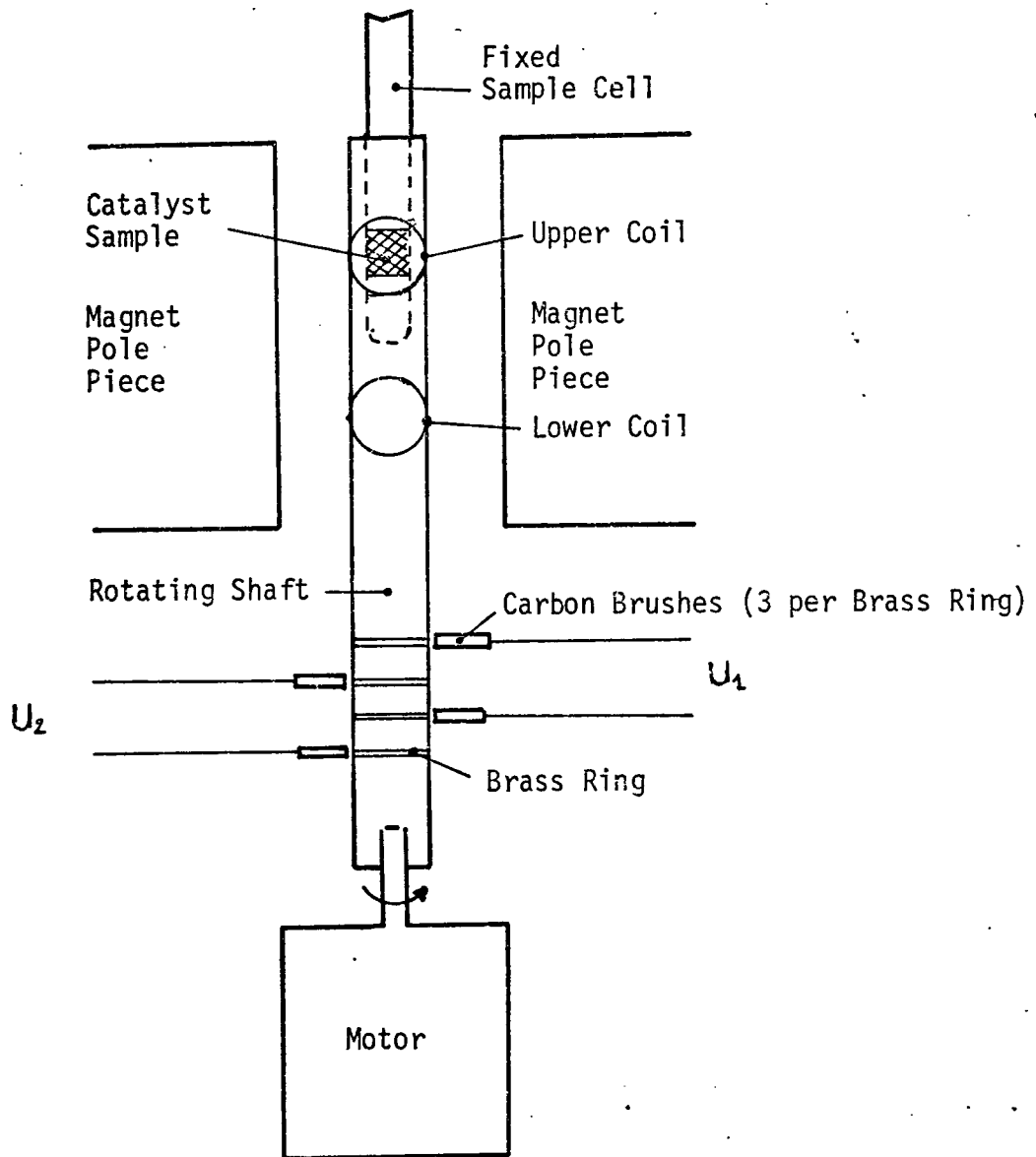


Fig. 33 Magnetometer Assembly

3. A balancing circuit was originally designed to zero the residual voltage between the reference and measuring coil when no sample was in. This complex electronic circuit was eliminated because it introduced unstabilities in the signal.

4. The filter band-pass originally set at 15-20 Hz has been narrowed to an 18-18 Hz sharp band. 18 Hz corresponds to the rotation frequency of the motor, and that is where the signal is maximum and noise free.

The band pass filter is a Krohn-Hite Model 3700R. The electro-magnet is a model 4800 Alpha Scientific magnet. The power supply for the magnet is a model 3003-1 Alpha Scientific type. The magnetic field was measured by a precision Gaussmeter (Model 620 Bell Gaussmeter). The measuring procedure used is the following: The field is set at the desired value (from 0 to 8000 gauss) and the differential signal is read on the digital volt meter. Then the sample cell is pushed in order to position the catalyst within the upper coil space. The length of the catalyst bed must not exceed 1 cm, otherwise a portion of the sample would be outside the coil space. Correct positioning is realized when signal is maximum on the voltmeter. This maximum is read and the sample pulled out of the field. The difference between the two signals with sample in and out gives a relative measure of magnetization in mv.

34. Sample Cell

The catalysts were treated (reduced, desorbed, calcined) in the same cell used for magnetic measurements, allowing in-situ measurements.

Two types of cells were used in this work. The first one is described in Fig. 341.

The cell described in the above picture has glass stoppers sealed on the inlet and outlet with grease. It could not withstand any increase in pressure over 2 psig due to a pressure drop across the catalyst bed. This was very inconvenient and a second type of cell was used for most of the experiments.

The second type of cell (Fig. 342) is closed at both ends by O-ring fittings capable of standing one atmosphere overpressure without any problem. In addition, its design results in increased space for the catalyst, hence increasing sensitivity.

The presence of the guard bed was necessary to prevent traces of oxygen from reaching the sample. After a few hours on a stream of argon or helium, a layer of contaminated catalyst was visible on top of the guard bed. An X-ray diffraction analysis revealed the greenish contaminated material to be mainly nickel oxide. A very small leak in the gas handling system is likely to be the cause of the problem. A pressure test indicated a slight drop of pressure (a fraction of a pound per square inch over a period of two hours) but the leak was never detected by means of a leak testing liquid.

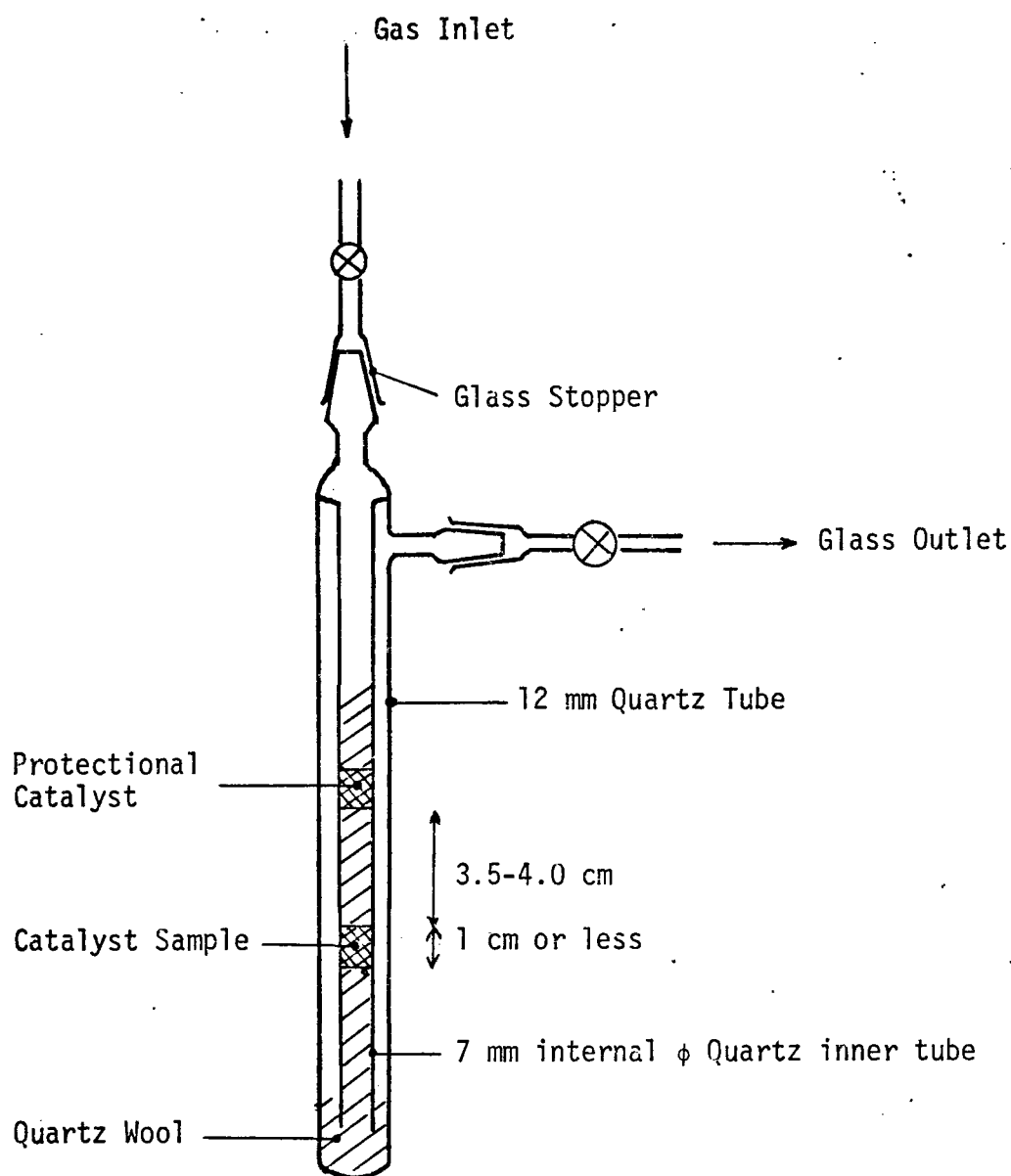


Fig. 341

Sample Cell - Type 1

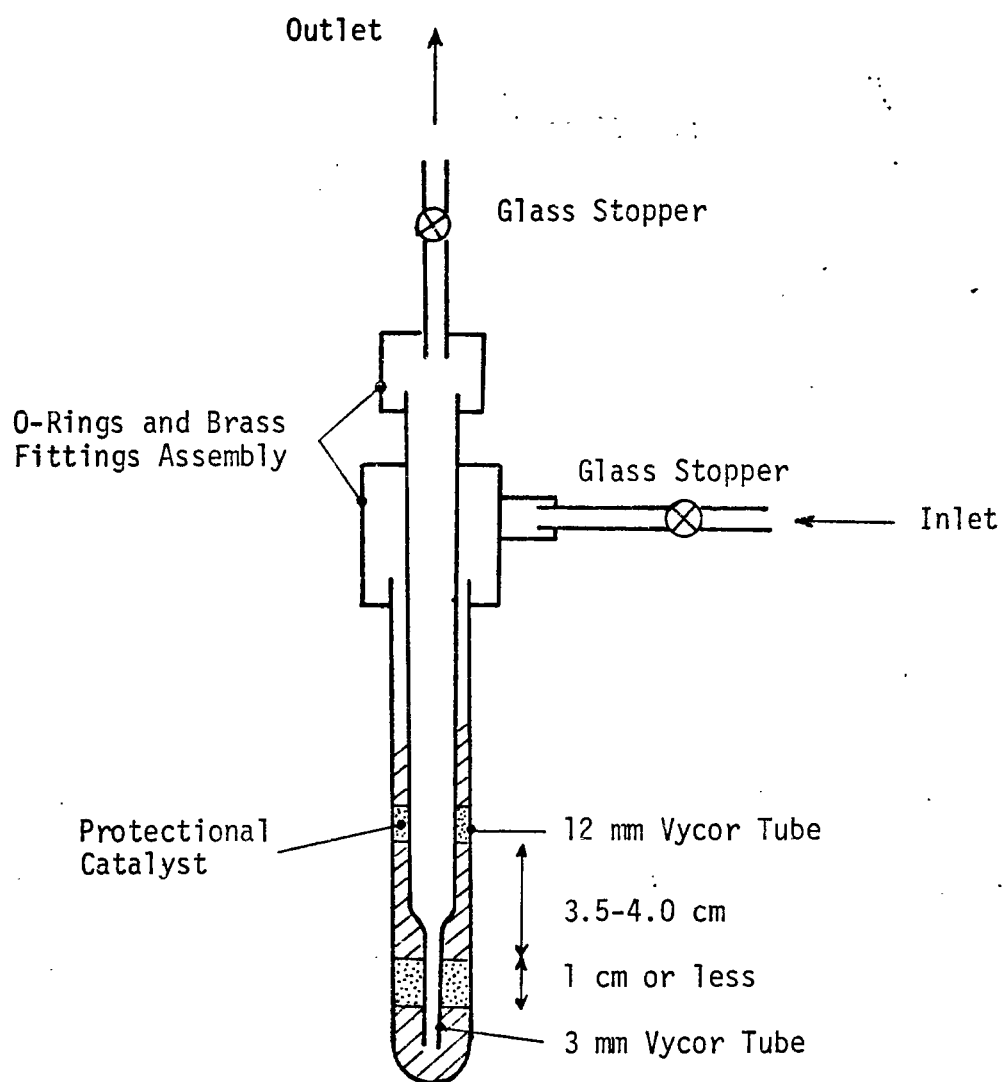


Fig. 342

Sample Cell - Type 2

This difficulty made in situ metallic surface area measurements questionable since the catalysts had to be outgassed in either argon or helium.

The guard bed was efficient in protecting the sample since after 20 hours on a stream of argon the sample did not show any decrease in magnetization.

35. Measurement of Saturation Magnetization

A sample containing small crystallites of nickel approaches saturation only at very high fields and very low temperatures. In the absence of high field or low temperature data, an alternate method was necessary to determine M_∞ .

This was done by sintering the samples in an inert atmosphere at high temperatures. The size of the nickel particles increased to an extent where the sample magnetically saturated even at low field. To check if the saturation was complete, a sample was sintered at 800°C for twelve hours in argon and then eighteen hours more at 850°C. There was no difference in the magnetization. The magnetization curve became flat rapidly (see Fig. 351). The last three points at 8.0-9.0 Kgauss are always slightly high due to non-uniformity in the field. For that reason, data points above 8.0 Kgauss were ignored in all magnetic measurements.

This procedure thus provides a value of M_∞ with a precision of the order of 5%. Such an error has been shown to have little effect on the final CSD.⁽¹⁾

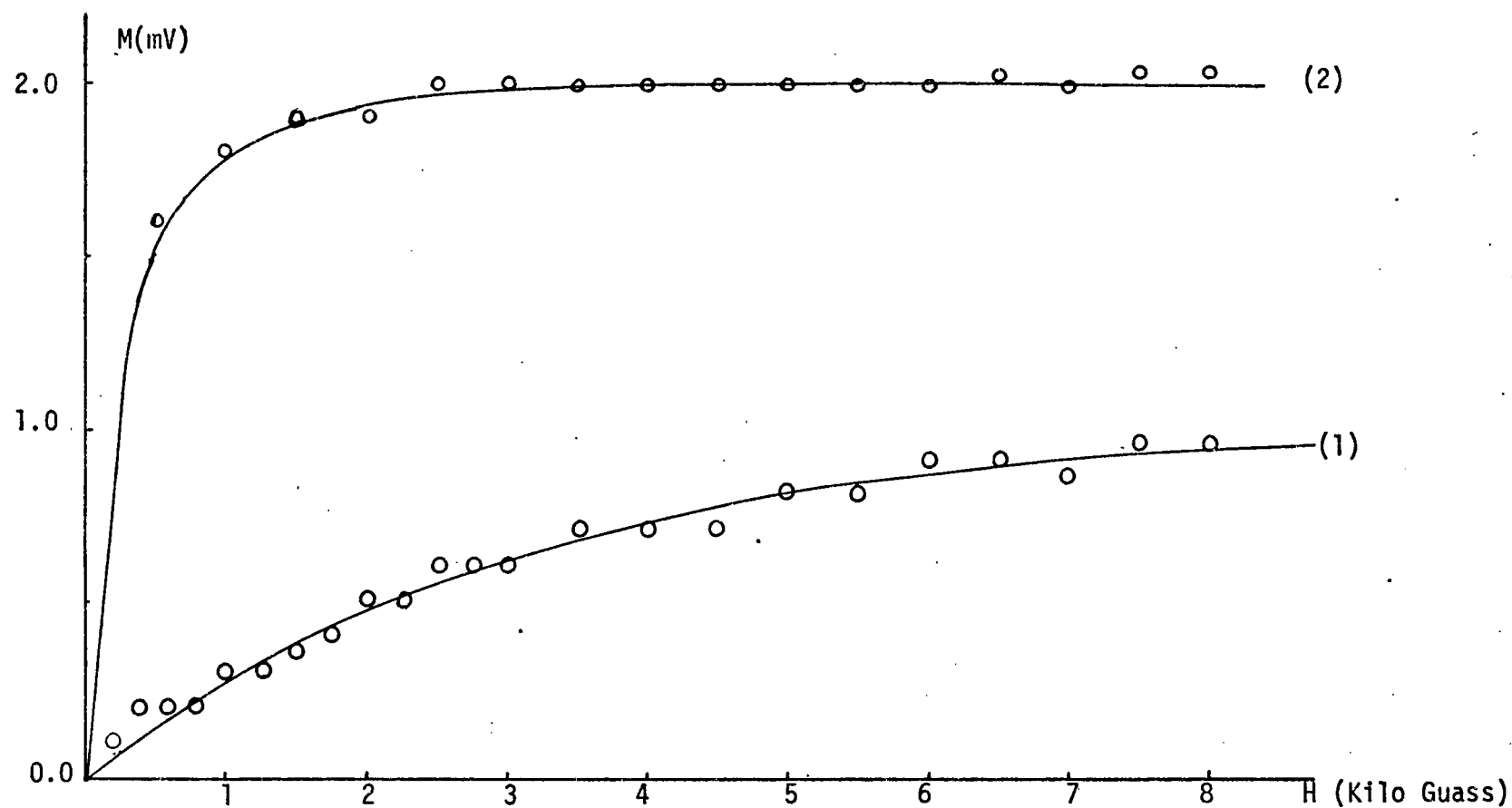


Fig. 351

Magnetization Curves for Catalyst 1 (219 mg)

(1) Reduced 4 hours at 500°C

(2) Sintered 12 hours in argon at 800°C and 18 hours at 850°C

It is interesting to note that after this sintering treatment, a sample becomes easier to reduce. A short reduction treatment in hydrogen at 400°C was performed on several sintered samples. These samples had been reduced originally at 400°C for fifteen to twenty hours. In all cases, reduction after sintering resulted in an increase of M_{∞} , showing additional reduced nickel.

36. Computation of the Reduced Nickel Content and Metallic Surface Area

If $g(r_i)$ are the calculated distribution coefficients, the surface area S can be calculated assuming a spherical shape for the nickel ^{hemi-}crystallites.

$$S = 2\pi \sum_{i=1}^n g(r_i) \bar{r}_i^2$$

where $\bar{r}_i$ is the average radius over the interval i and $g(r_i)$ the percentage of particles in that interval. The volume of the nickel is

$$V = \frac{2\pi}{3} \sum_{i=1}^n g(r_i) \bar{r}_i^3$$

With $S = 8.91 \times 10^6$ gm/m³ as the density of nickel we get:

$$S = \frac{3 \sum_{i=1}^n g(r_i) \bar{r}_i^2}{8.91 \times 10^6 \sum_{i=1}^n g(r_i) \bar{r}_i^3} \text{ m}^2/\text{gm of nickel}$$

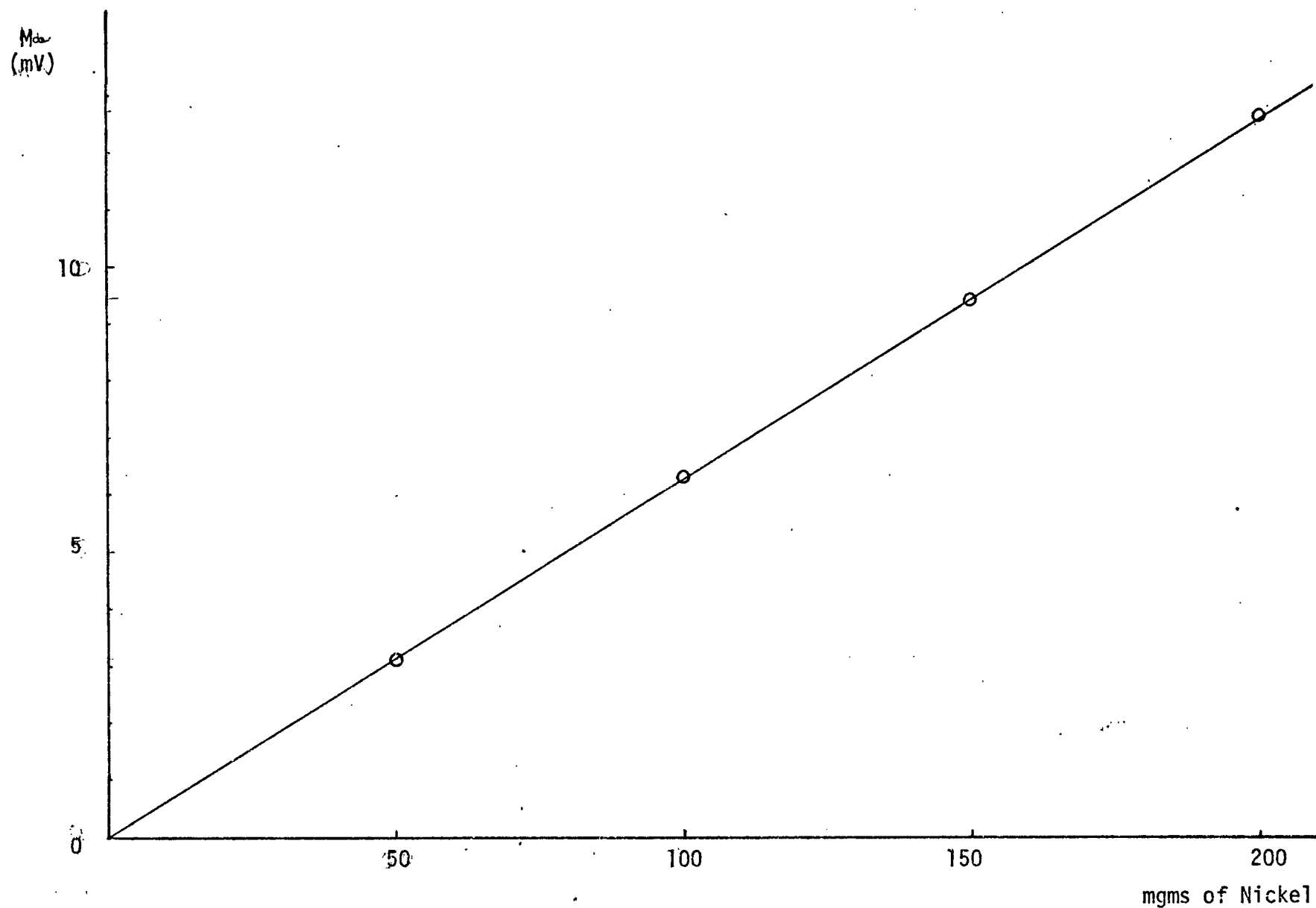


Fig. 36 Calibration Curve M_{∞} vs. Mass of Nickel

The amount of reduced nickel can be deduced from the value of M_{∞} and a calibration curve. The fact that M_{∞} is proportional to the mass of nickel at constant temperatures results from the accepted assumption that I_{sp} the spontaneous magnetization depends only on temperature.⁽²⁰⁾ The calibration curve was obtained from a nickel powder. No detectable nickel oxide was found from an X-ray analysis. The powder is bulk nickel covered with a very thin layer of protective nickel oxide. The saturation magnetization of weighed samples is given in Fig. 36.

4. CATALYST PREPARATION TECHNIQUE

41. Materials

Deionized Water

Nickel Nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ Reagent Grade

Urea H_2NCONH_2 Reagent Grade

Support Silica* (Cab-O-Sil HS5)

γ -Alumina** (Catapal SB, activated)

42. Apparatus

The reaction vessel is a 2.0 liters three-neck Pyrex flask. It is equipped with a stirring rod on the central neck, a thermocouple and thermometer on one of the side necks. The thermocouple is connected to the temperature controller. The remaining side neck is used to introduce the urea. The temperature controller regulates the temperature of the solution by means of a heating mantle. The pH can be measured by a Lazar pH-converter used with a combination glass electrode (Ag-AgCl reference).

43. Procedure

The required weights of solid nickel nitrate and support are dissolved in the water and the stirred suspension is brought to 90°C. When temperature is steady, the reaction is started by adding the solid urea.

$$*S(\text{BET}) = 325 \text{ M}^2/\text{gm}$$

$$**S(\text{BET}) = 250 \text{ M}^2/\text{gm}$$

To stop the reaction, the temperature controller is turned off and the heating mantle removed, but the stirring is continued until the suspension has cooled to room temperature. The suspension is then filtered on a Buchner funnel and the green precipitate is replaced into the reaction flask, where it is washed by stirring with 800 ml of hot water for a few minutes before filtering. Washing is repeated two times and the precipitate dried in an oven at 120°C overnight. Finally, the dry catalyst is crushed and sieved to less than 60 mesh particles (250 microns or less).

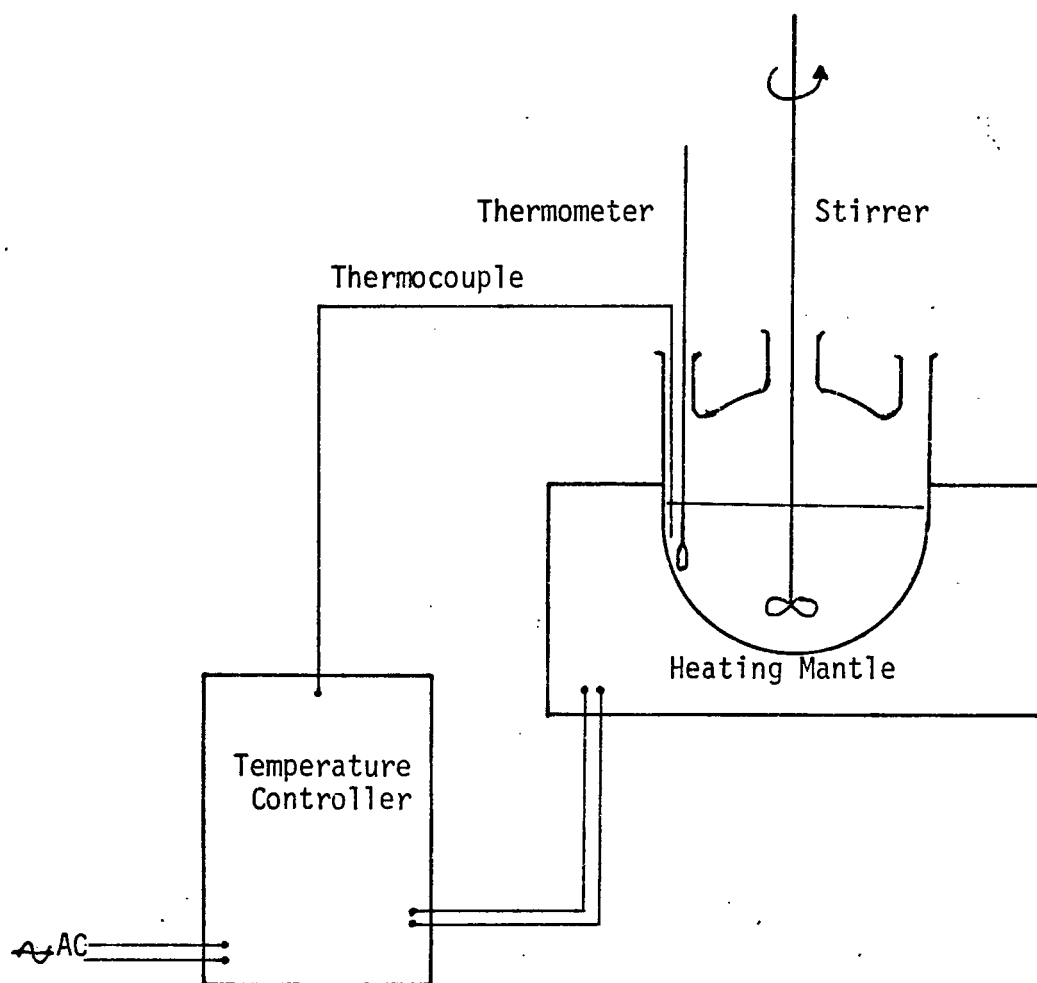


Fig. 42 Sketch of Apparatus Used in Catalyst Preparation

5. DETERMINATION OF TOTAL NICKEL CONTENT IN THE CATALYSTS

The catalysts supported on silica were dissolved and the nickel solution separated from the support by filtration. The nickel concentration was then measured by colorimetry. The procedure, which does not apply when alumina is used as a support, is described below.

51. Dissolution of the Sample

The procedure is that used by Linsen⁽¹⁸⁾ for nickel on silica catalysts prepared by co-precipitation.

A sample of the dry catalyst containing about 150 mgs of nickel is weighed and placed in a 100 ml beaker. Five ml of concentrated hydrochlorhydric acid are added and the solution is evaporated to dryness. The residue is extracted by 100 ml of 1:1 hydrochlorhydric acid. The solution is filtered, transferred to a 100 ml volumetric flask and diluted to the mark with deionized water.

52. Colorimetry of the Solution

The solution containing the Ni^{++} and Cl^- ions is titrated using a spectro-colorimeter (Bausch & Lomb Spectronic 20). Nickel adsorbs at a wave length of 390 milli microns.⁽¹⁹⁾ For each catalysts, two samples were dissolved and titrated to check the reproducibility. In all cases, the agreement was very good.

53. Standard Solutions

For quantitative information, standard solutions are necessary. They were prepared from a known quantity of nickel nitrate or metallic nickel powder, treated exactly as described in Section 41.

To ensure that the chlorine ions do not interfere, HCl was replaced by nitric acid in two cases. Four sets of standard solutions were thus obtained:

Nickel nitrate dissolved in nitric acid

Nickel nitrate dissolved in hydrochlorhydric acid

Nickel powder dissolved in nitric acid

Nickel powder dissolved in hydrochlorhydric acid

The four calibration curves obtained at 390 mμ are given in Appendix B. The agreement is very good, showing the non-interference of Cl^- or NO_3^- ions with the adsorbance at 390 mμ.

6. PREPARATION CONDITIONS AND TOTAL NICKEL CONTENT OF THE UNREDUCED CATALYSTS

<u>Catalyst No.</u>	<u>Support</u>	<u>Reactants</u>	<u>Reaction Time (hours)</u>	<u>Total Nickel Content wt % Nickel</u>
1	Silica	(1) ^B	4	17%
2	Silica	(1)	4	25%
3	Silica	(1)	4	30%
4	Silica	(1)	8	31%
5	Silica	(1)	14	37%
6	Silica	(1)	20	36%
7	Silica	(2)	4	34%
8	Silica	(2)	8	40%
9	Silica	(2)	14	40%
10	Al ^v mina	(2)	4	21%*
11	Alumina	(2)	14	34%*

(*) Determined from the saturation magnetization of a sample reduced at 800°C (see Section 36). At this temperature, nickel is practically totally reduced.⁽²⁸⁾

The amounts of reactants used as described in Section 4 were the following:

(1) 1.0 l deionized water
 40.70 gm Nickel Nitrate
 7.6 gm Support
 25.24 gm Urea $\rightarrow$ $\text{NH}_2\text{CO NH}_2$

(2) 1.0 ℓ deionized water
 81.4 gm Nickel Nitrate
 10.0 gm Support
 50.48 gm Urea

(1)^B Same as (1) except that 2-3 ml of
 1:2 nitric acid were added before the
 reaction started to bring initial pH
 down to 2.5.

In terms of concentration, the above compositions correspond to

(1) Nickel Nitrate 0.14 M ✓
 Urea 0.42 M
 Support 7.6 gm/ ℓ

(2) Nickel Nitrate 0.28 M
 Urea 0.84 M
 Support 10 gm/ ℓ

7. SAMPLE PREPARATION - REDUCTION AND PRETREATMENT CONDITIONS

A sample of the catalyst is weighed (precision ± 0.5 mg) and loaded in a sample cell described earlier (Fig. 341 and 342). Depending on the bulk density of the catalysts, sample weights ranged from 200 to 800 mg approximately.

The sample cell is then connected to the gas handling system and a sleeve furnace positioned around the sample. The hydrogen (High Purity Grade) is set at the desired flow-rate for reduction and the temperature raised to the reduction temperature at a rate of about eight degrees/minute.

When the reduction is complete, the sample is outgassed in argon or helium (both High Purity Grade) for one hour at 25-30 degrees above the reduction temperature in order to remove any adsorbed hydrogen. Finally, it is cooled to room temperature with the inert gas still flowing. This procedure has been found to be sufficient to clean the surface of nickel on alumina catalysts in the past.⁽²¹⁾

The sample cell is then isolated from the atmosphere by closing the inlet and outlet valves and transferred to the magnet. The magnetization of the sample is measured at room temperature for twenty values of the applied field following the procedure in Section 34. The sample cell is reconnected to the gas handling system for additional treatment.

When connecting the valves back to the gas lines (especially the inlet line), a small quantity of air trapped in the dead volumes could

possibly contaminate the sample, even though the connection was made with argon flowing. For this reason, the sample is further reduced at 350°C for one hour and outgassed as before. This is a safety measure to reduce any possible layer of oxygen on the catalyst, although a test indicated that no measurable loss of magnetization occurred during the procedure. The protectional catalyst stops any small amount of oxygen before it contaminates the sample itself located downstream.

The sample is finally severely sintered at 800-900°C in flowing argon for about twelve hours. The magnetization of the sintered sample is taken at room temperature to obtain the saturation value (Section 35). To summarize a typical experiment involved the following steps:

1. Sample reduction in flowing hydrogen at T°C.
2. Cleaning in argon (or He) at T + 25°C for one hour.
3. Taking magnetization data at room temperature.
4. Reduction at 350°C in hydrogen for one hour and cleaning as above in argon.
5. Sintering at 800-900°C in flowing argon for 12 hours.
6. Taking saturation magnetization data at room temperature.

Note that all reduction temperatures were 400°C or higher so no further reduction took place during Step 4.

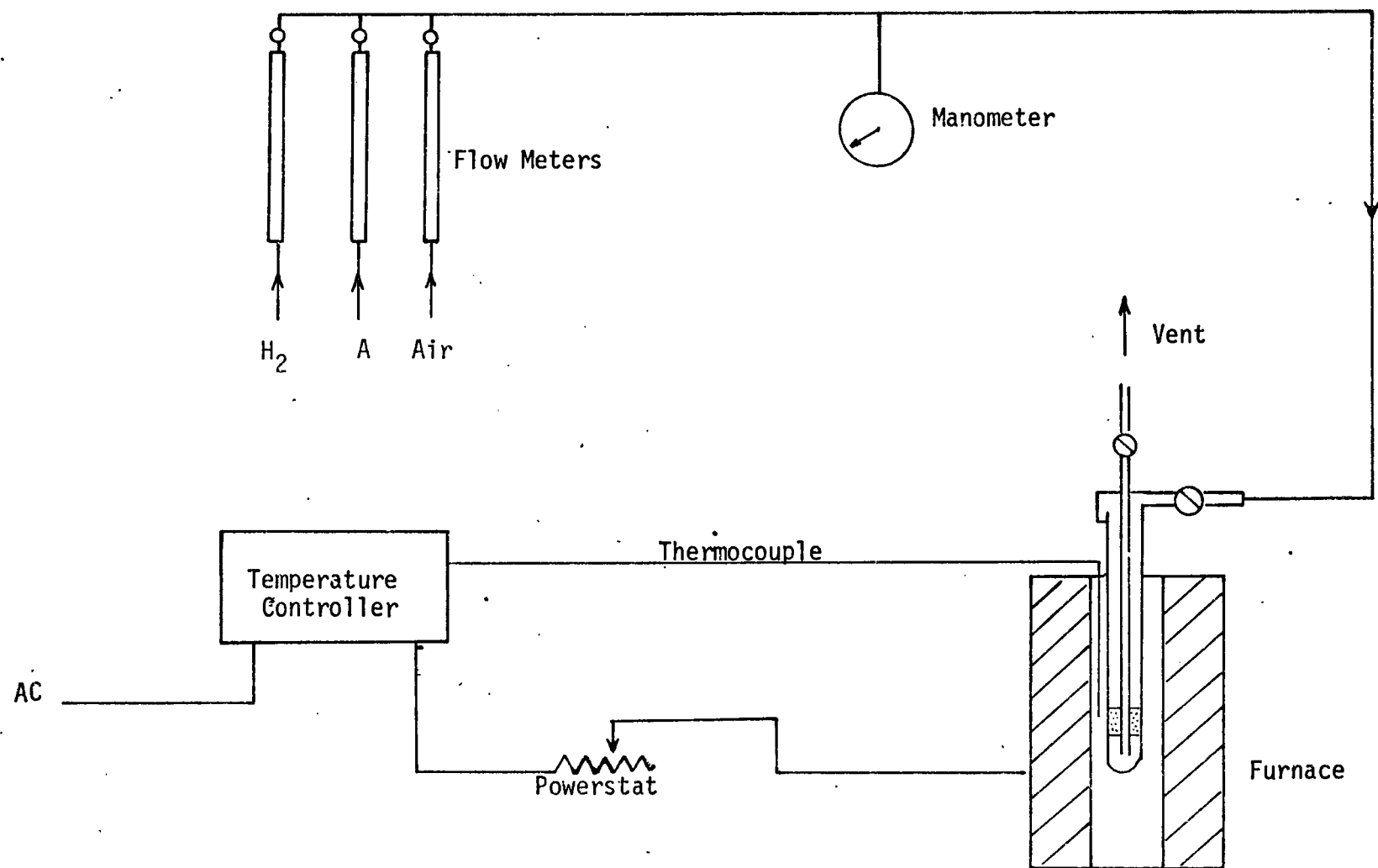


Fig. 7 Gas Handling System and Temperature Control

8. RESULTS AND DISCUSSION

81. Effect of Preparation Variables

In this section, the effect of some preparation parameters on the dispersion of the catalysts is investigated. They include the precipitation time, composition of the solution, nature of the support, initial pH of the solution. For each experiment, the magnetization data can be found in Appendix D along with the exact values for the CSD coefficients calculated from these data.

811. Precipitation Time

Catalysts 2, 4, 5, and 6 have been prepared in the same way except with a precipitation time of 4, 8, 14 and 20 hours, respectively. The total amount of nickel in each catalyst is recalled in Table 811 together with other information.

Figures 8111 to 8114 show the CSD for these catalysts after 15 to 20 hours of reduction at 400°C in flowing hydrogen (25-30 cc/mm).

Figure 8111 shows three different CSD's. One is the original (full lines). Another distribution (dotted lines) was obtained after changing the experimental value of M_{∞} by about 10%. The last one (dots) is the distribution calculated from the M-H curve drawn in a different way (by hand). The results show that the CSD calculated is only slightly sensitive to experimental error on M_{∞} and to the

manner in which the M-H curve is drawn. The last check was necessary since some scattering in the experimental measurements of magnetization is inevitable.

The smaller peak appearing in Fig. 8111 and 8112 has no quantitative meaning. Model calculations (see Section 32) have clearly shown the inability of the computation method to account quantitatively for these crystallites less than $10 \text{ \AA}$ in radius. They also showed that if any of these crystallites are present in the model, they will be found also in the calculated distribution, but at the wrong place. The smoothed curve drawn on Fig. 8111 represents what the actual CSD may look like.

Catalyst 2 exhibits a sharp peak at $17.5 \text{ \AA}$. However, at higher precipitation times, the CSD becomes broader and the surface area decreases.

Catalyst Number	Total Nickel Content (wt%)	Reduction Conditions	Degree of Reduction	Metallic Surface Area (M^2/gm)
2	25%	20 h @ 400°C	33%	171
4	31%	18 h @ 400°C	29%	140
5	37%	15 h @ 400°C	32%	127
6	36%	15 h @ 400°C	35%	126
7	34%	15 h @ 400°C	45%	144
8	40%	15 h @ 400°C	54%	143
9	40%	15 h @ 400°C	69%	132.5

Table 811

Characteristics of the Catalysts whose CSD are given in Figures 8111 to 8117

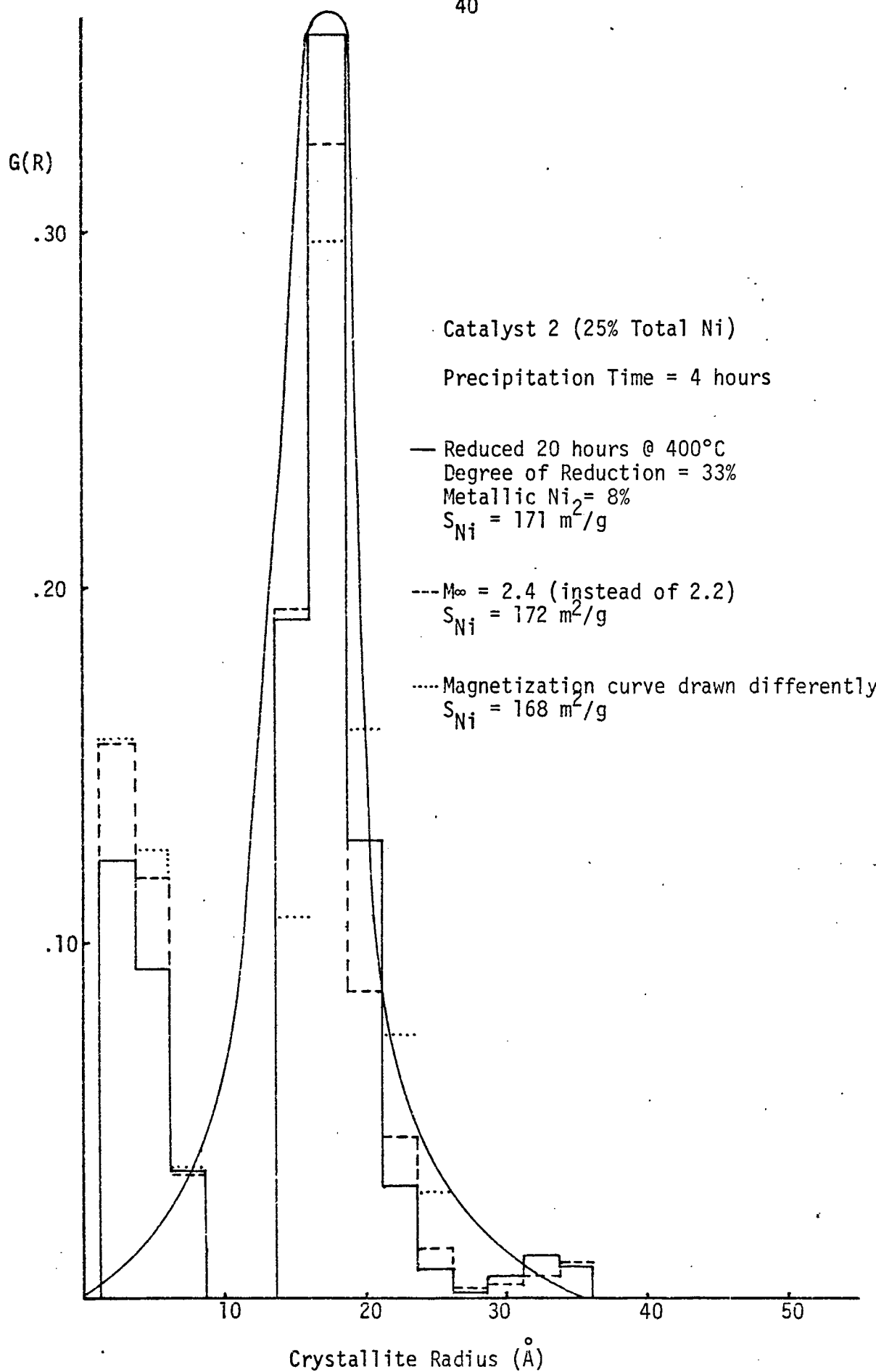


Fig. 8111

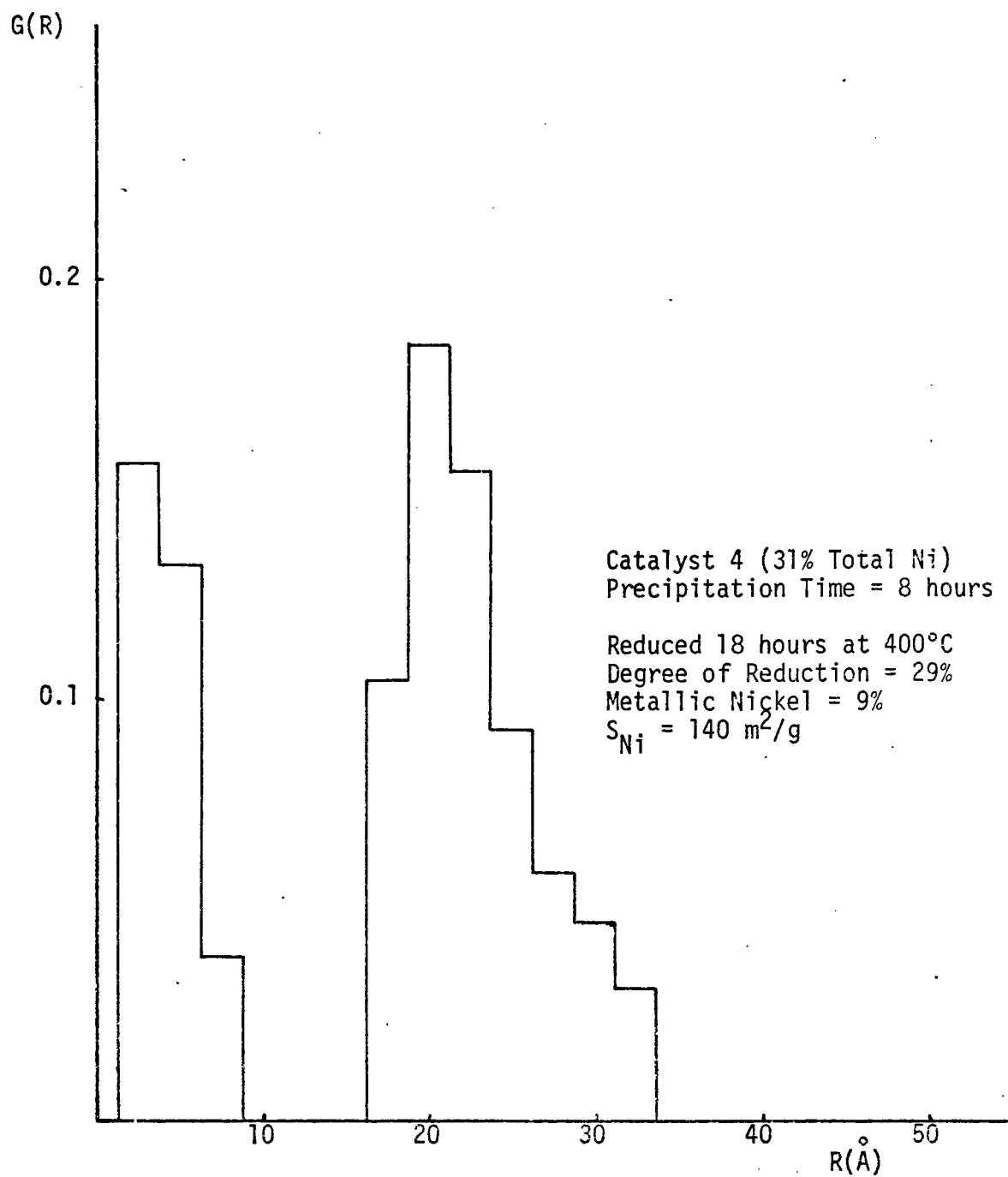


Fig. 8112

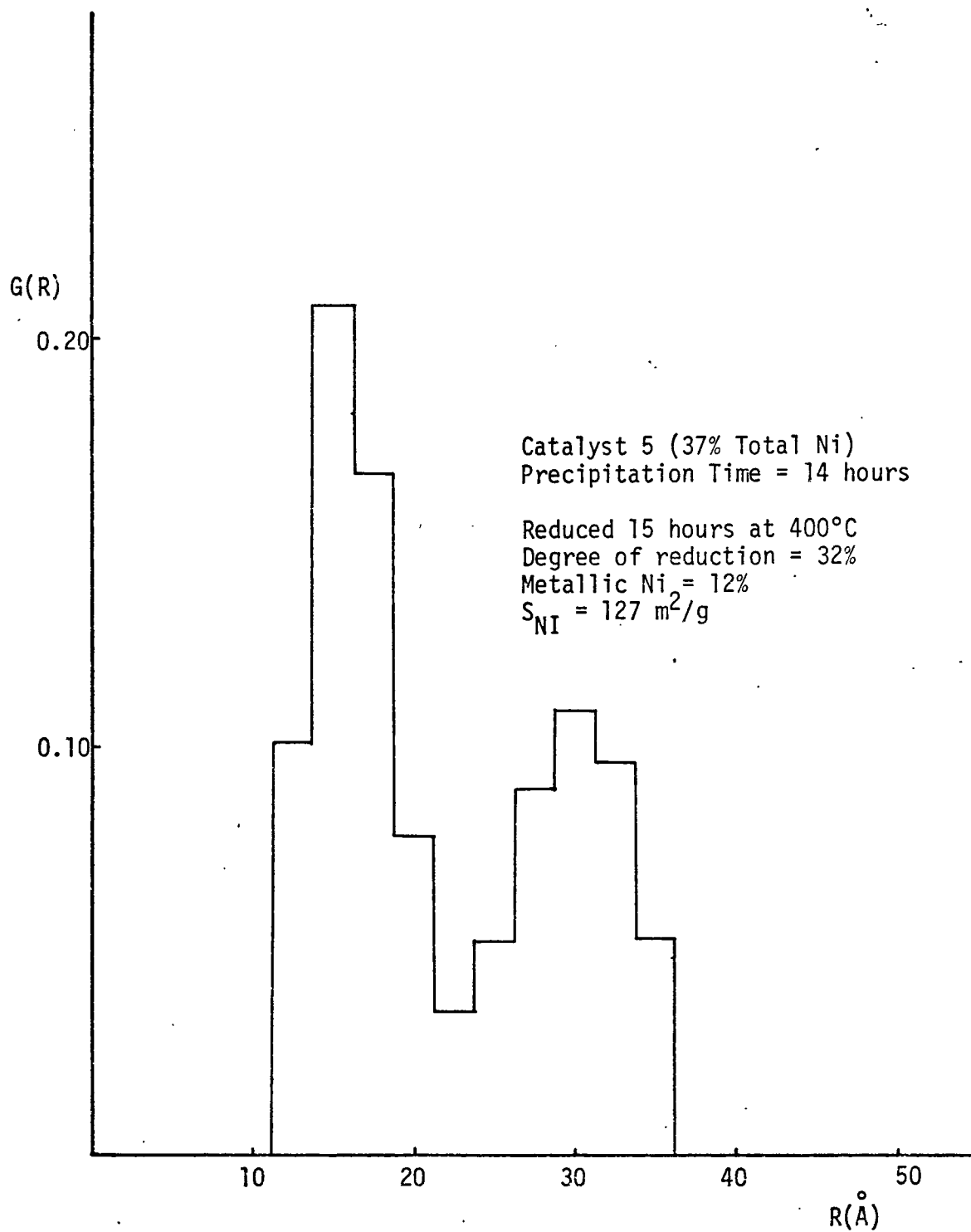


Fig. 8113

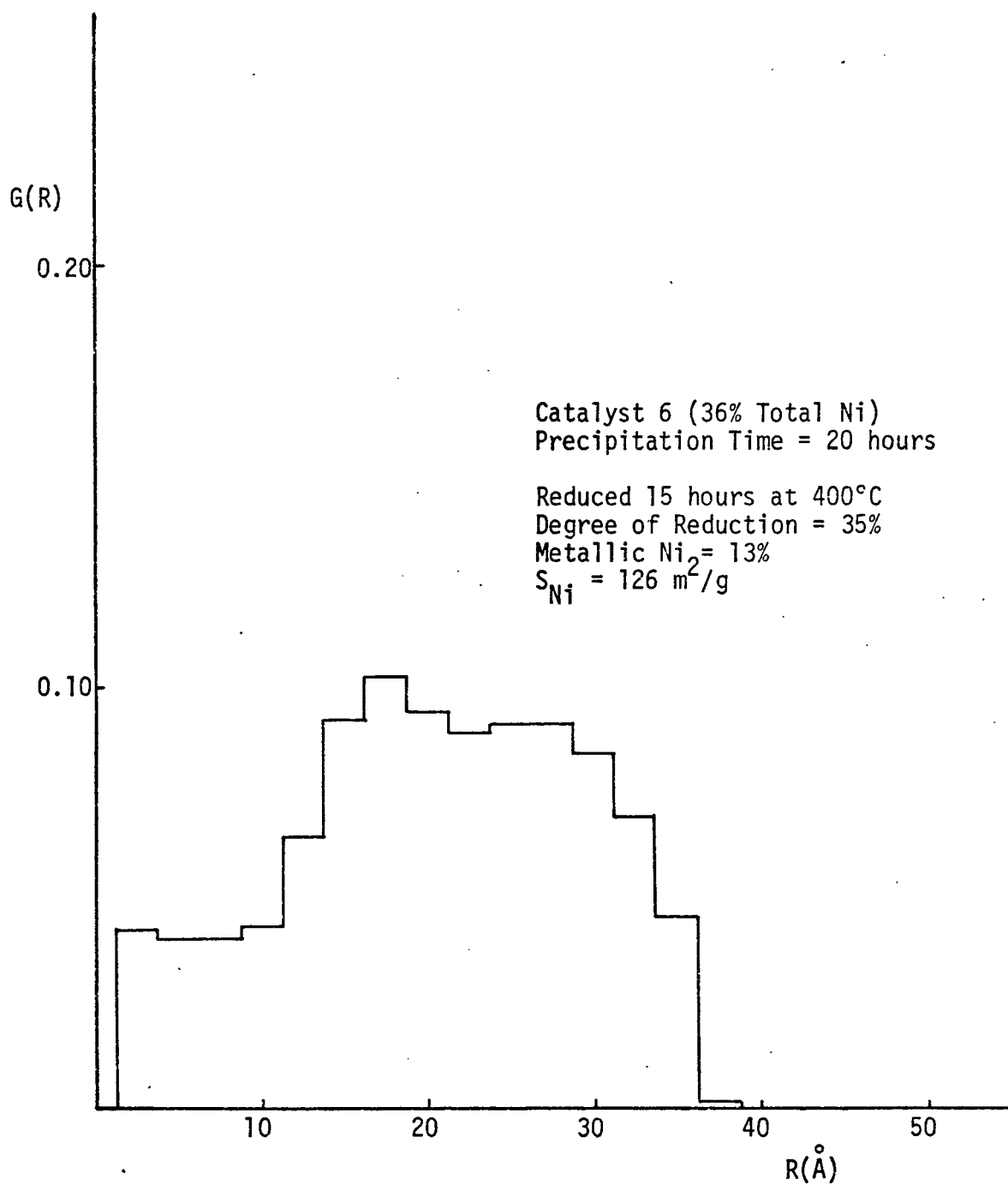


Fig. 8114

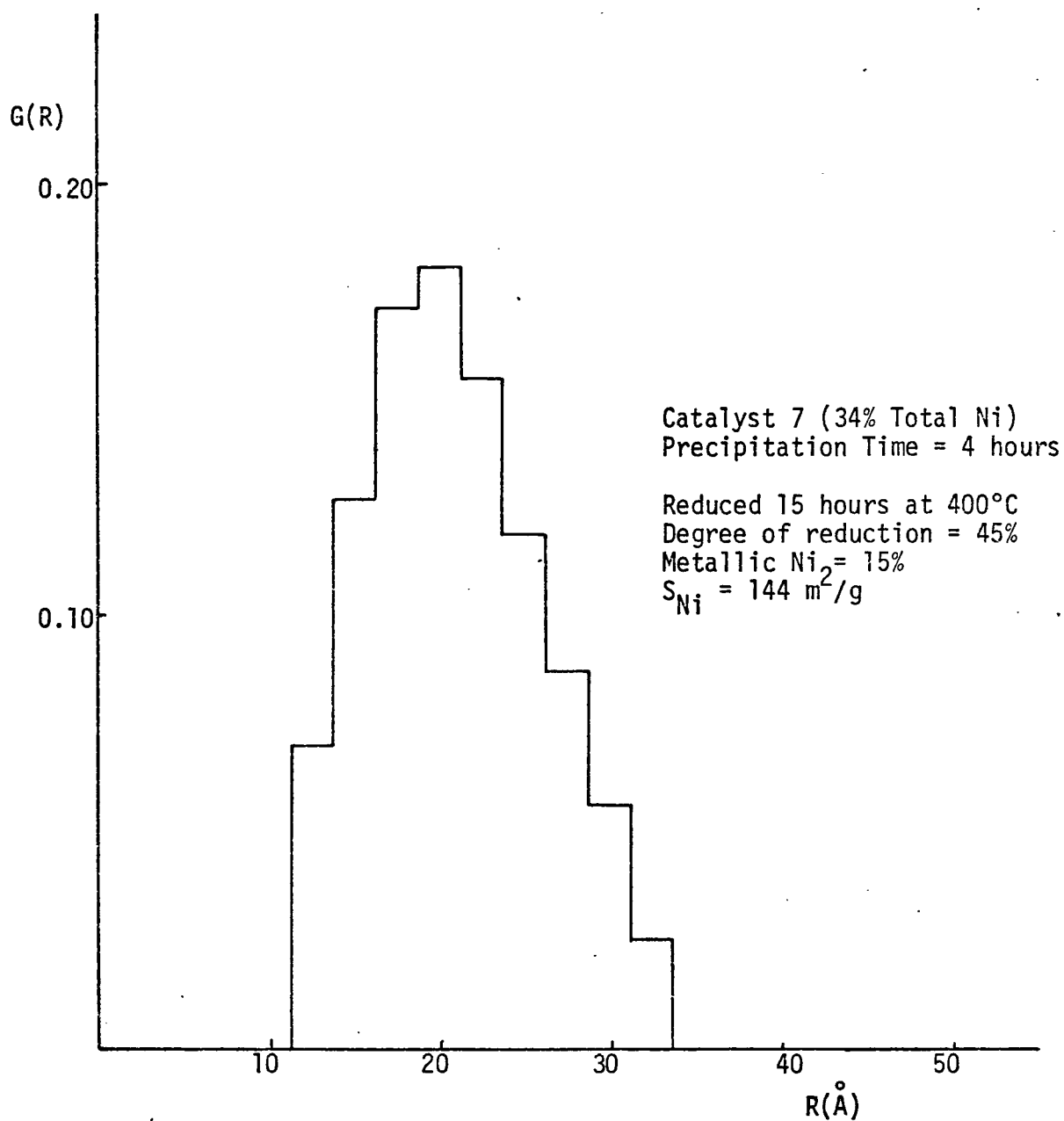


Fig. 8115

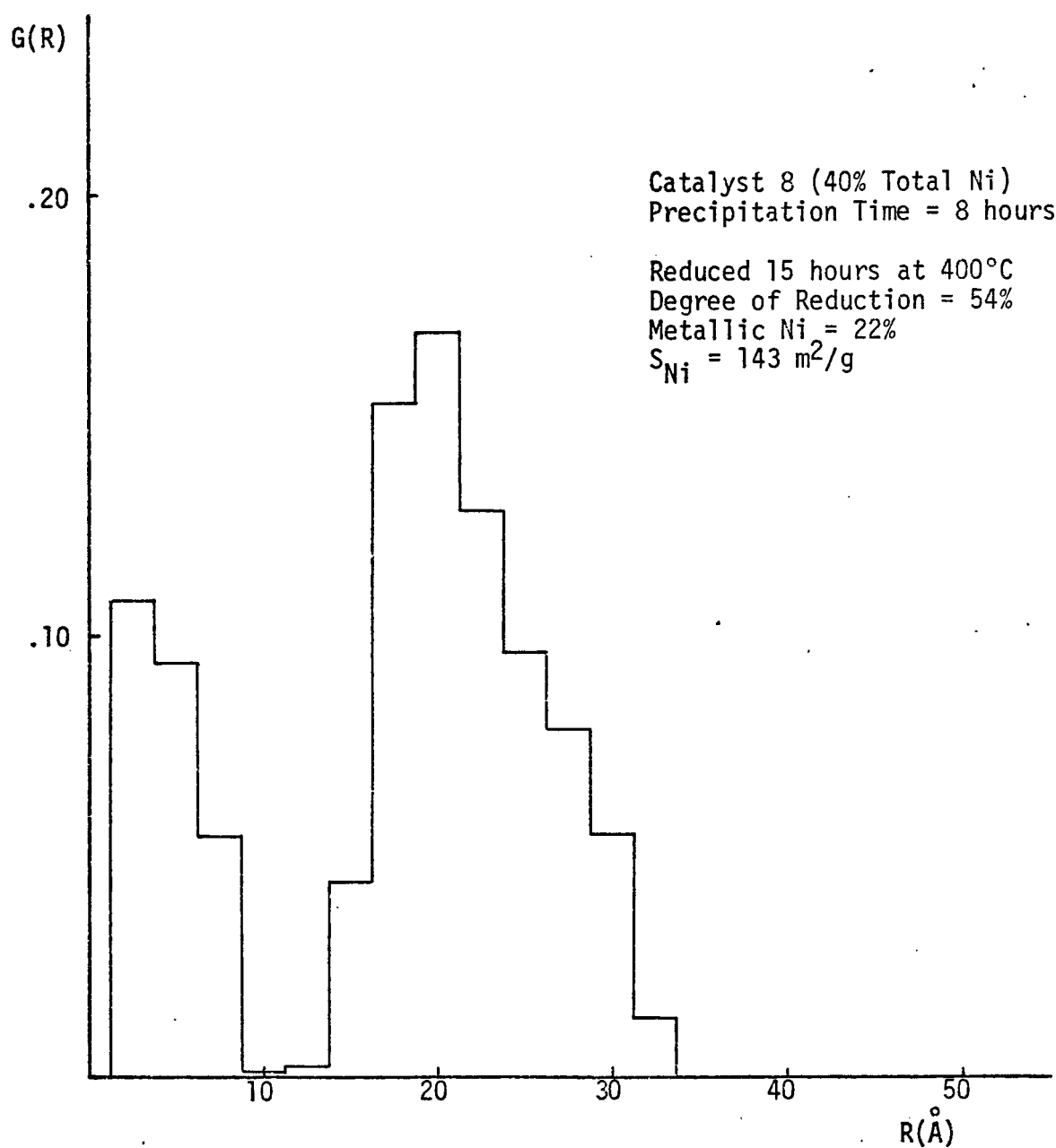


Fig. 8116

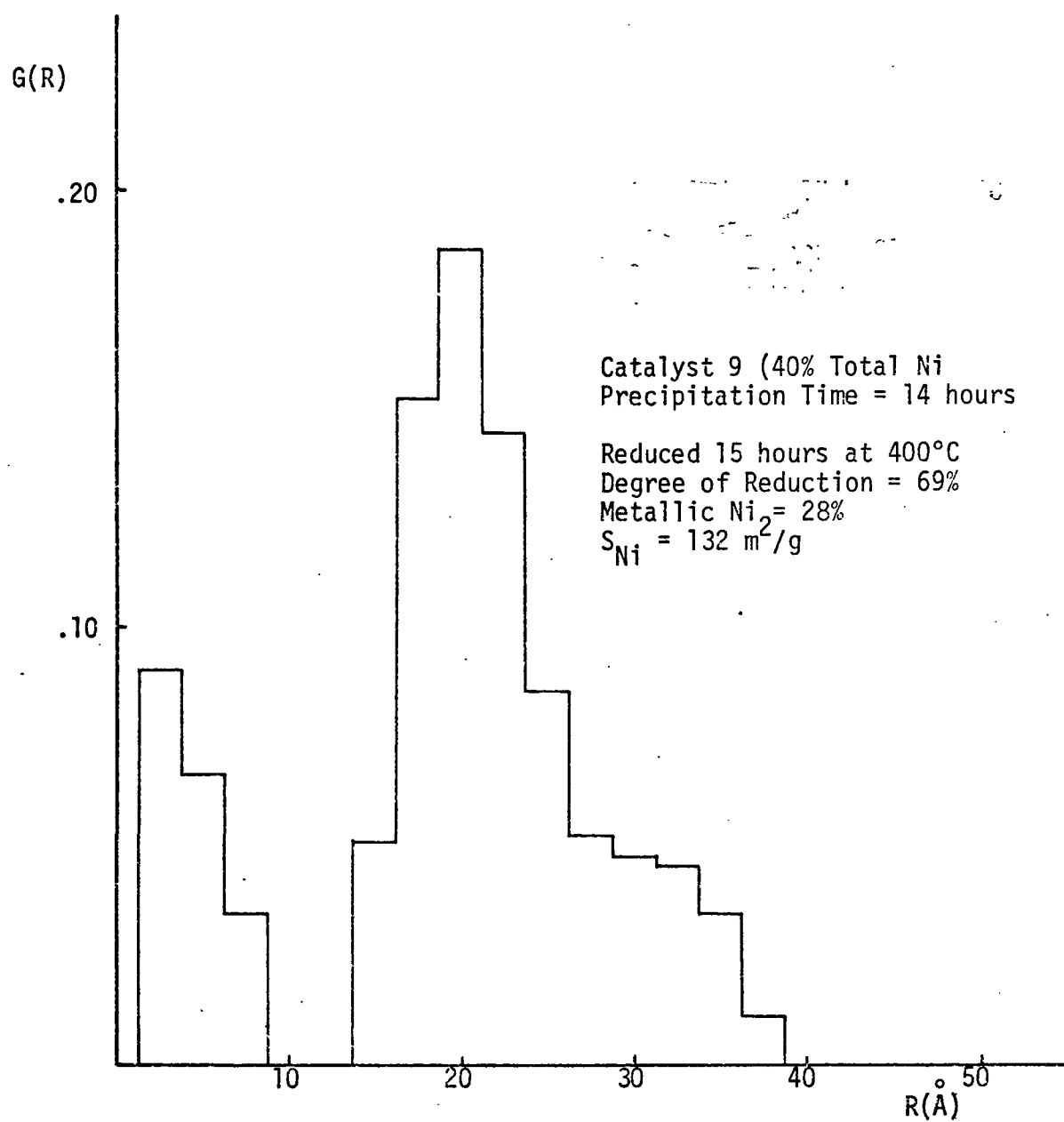


Fig. 8117

Another series of catalysts with identical preparation parameters was 7, 8 and 9. Their precipitation time was 4, 8 and 14 hours, respectively. They differ from the first series (catalyst 2, 4, 5) in the composition of the solution (twice as concentrated in urea and nickel nitrate as the solution used for the first series). For this second series of catalysts, increased precipitation time did not affect the dispersion as much as it did for the first series, as it can be seen from Figs. 8115 to 8117. Still there is a trend towards lower surface area and broader CSD upon increasing the precipitation time.

It is expected that the precipitation time should be less critical when the precipitating reactants are more concentrated, because the precipitation lasts longer. But it is significant also that catalysts 8 and 9 (8 and 14 hours precipitation time) had lower density and resistance to crushing compared to the more compact structure of catalysts 7, 2 and others. It is possible that a structural change of the support may be responsible for masking the effect of a prolonged precipitation. This change in the structure of the silica will be further discussed in Section 816 since it may be a desirable effect.

812. Composition of the Solution

Catalysts 2 and 7 were prepared at the same conditions except that the composition of the solution was different. This is also true for catalysts 4 and 8, and 5 and 9. Exact compositions are given in Section 6.

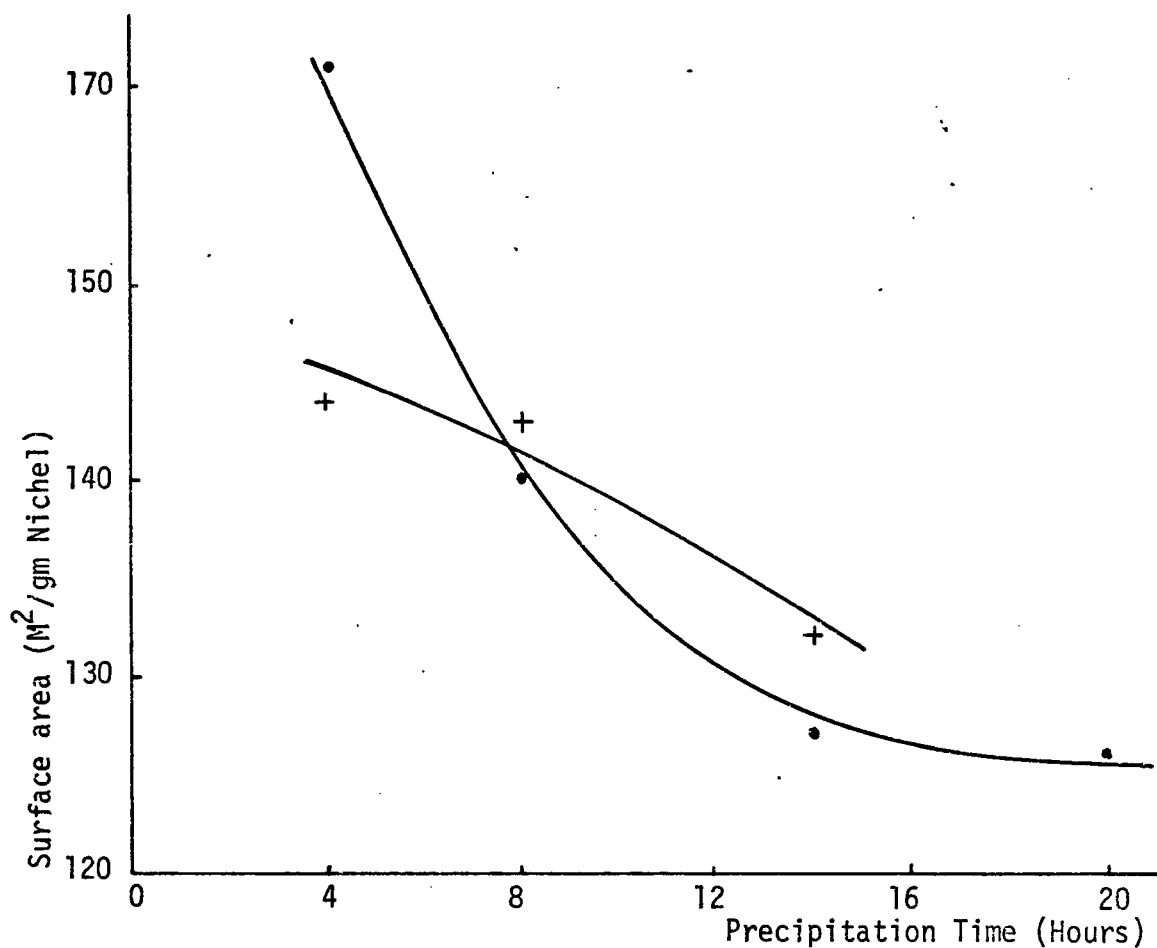


Fig. 812 Influence of Precipitation Time and Composition on the Surface Area - All Catalysts Reduced in Similar Conditions.
 Dots refer to composition (1): 0.14 M nickel nitrate, 0.42 M urea, 7.6 gm/l silica.
 Crosses refer to composition (2): 0.28M nickel nitrate, 0.84 M urea, 10 gm/l silica.

Comparing Figs. 8111 and 8115, the CSD is broader for catalyst 7 (more concentrated solution) than it is for catalyst 2. The precipitation time for these catalysts was 4 hours.

At 8 hours precipitation time, the composition of the solution has apparently not much effect on the dispersion (compare Fig. 8112 and 8116).

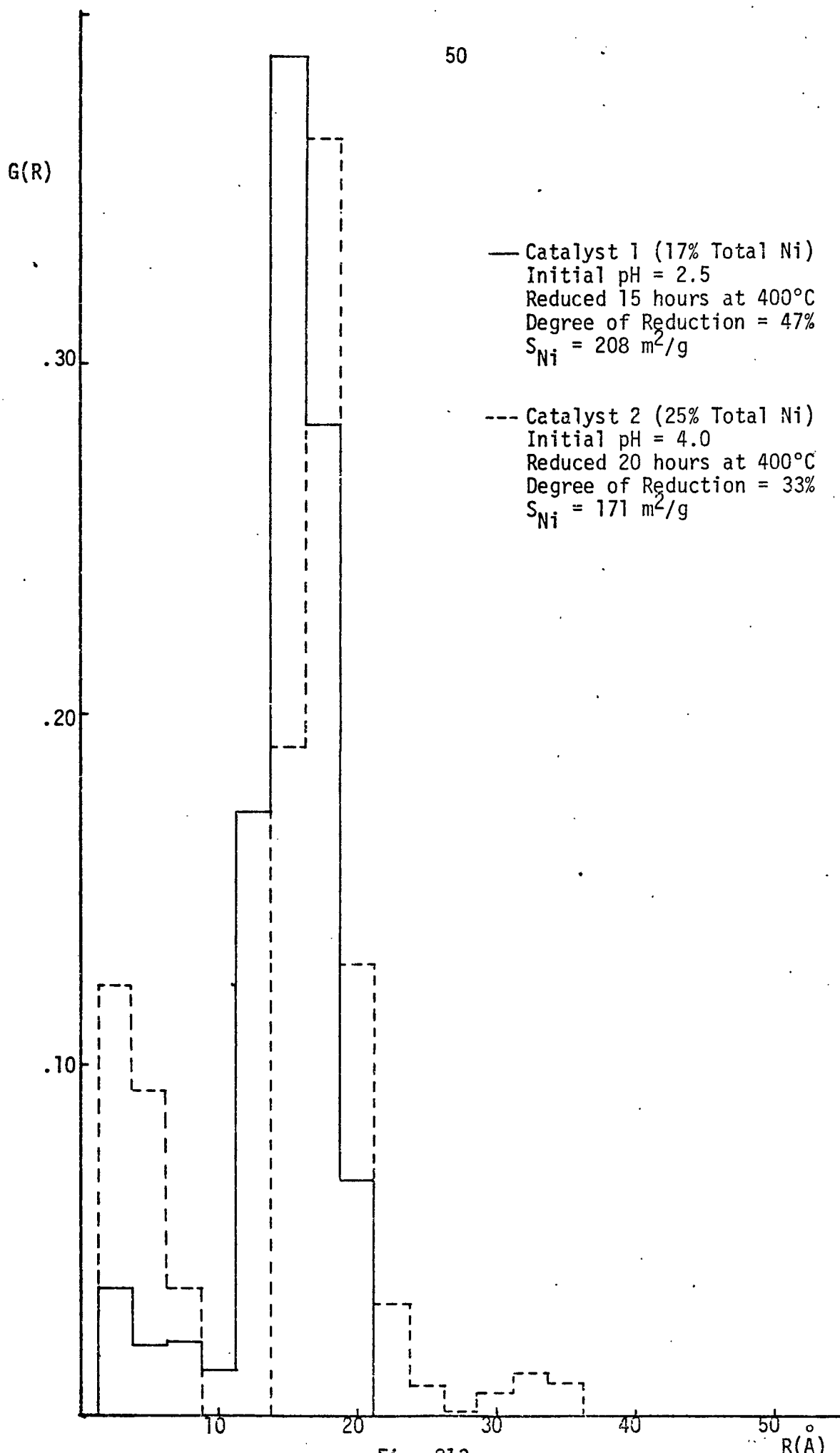
After 14 hours precipitation, the catalyst originated from the more concentrated solution (Cat. 9, Fig. 8117) shows even a higher surface area than the one prepared with lower nickel and urea concentrations (Cat. 5, Fig. 8113).

Fig. 812 illustrates the fact that the surface area of a catalyst prepared from the solution (1) decreases relatively more upon increased precipitation time than it does when the solution (2) is used.

The observations in Section 811 and 812 indicate that it is detrimental both to the uniformity of the crystallite sizes and the surface area to increase the load of nickel either by longer precipitation times or higher concentrations of reactants. This is in agreement with the generally accepted observation that dispersion decreases with increased nickel loading in a given series of catalysts.

813 Effect of the pH Prior to Precipitation

The pH has to be less than about 5.5 before the urea is added to the solution in order to prevent premature precipitation of the nickel. This condition was always followed with the compositions used. Initial pH was about 4.0 at 90°C. One batch was made using a lower initial pH



of 2.5 by adding a few ml of dilute nitric acid to the solution before precipitation. The resulting catalyst 1 had 17 wt% nickel after a 4 hours precipitation time.

Its counterpart catalyst 2 (same preparation conditions but initial pH = 4.0) contains more nickel (25%) than catalyst 1. The effect of starting from a more acid solution undoubtedly delays the precipitation, thereby reducing the loading at similar reaction times.

The CSD for these two catalysts are compared on Fig. 813. Both have been reduced at 400°C in hydrogen (25-30 cc/mn). Catalyst 1 was reduced 15 hours and catalyst 2 20 hours. The difference in the surface areas ($208 \text{ M}^2/\text{gm}$ and $171 \text{ M}^2/\text{gm}$) between catalyst 1 and 2 is significant and cannot be ascribed to the difference in reduction times (see Section 822). Catalyst 1 has a narrow CSD with a maximum at $15 \text{ \AA}$ compared to $17.5 \text{ \AA}$ for catalyst 2. The effect of the initial pH seems to be a decrease in the nickel content, with expected higher surface area and better uniformity in crystallite sizes.

814 Nature of the Support

Among all preparation variables, the nature of the support is one which promises to be critical for the characteristics of the catalyst. It was found that substituting γ -alumina for silica had a disastrous effect on the dispersion of nickel.

Catalyst 10 was prepared similar to catalyst 7 and catalyst 11 to catalyst 8, except that 10 and 11 are alumina-supported. After reduction at 400°C, the CSD for these catalysts are given on Fig. 8141

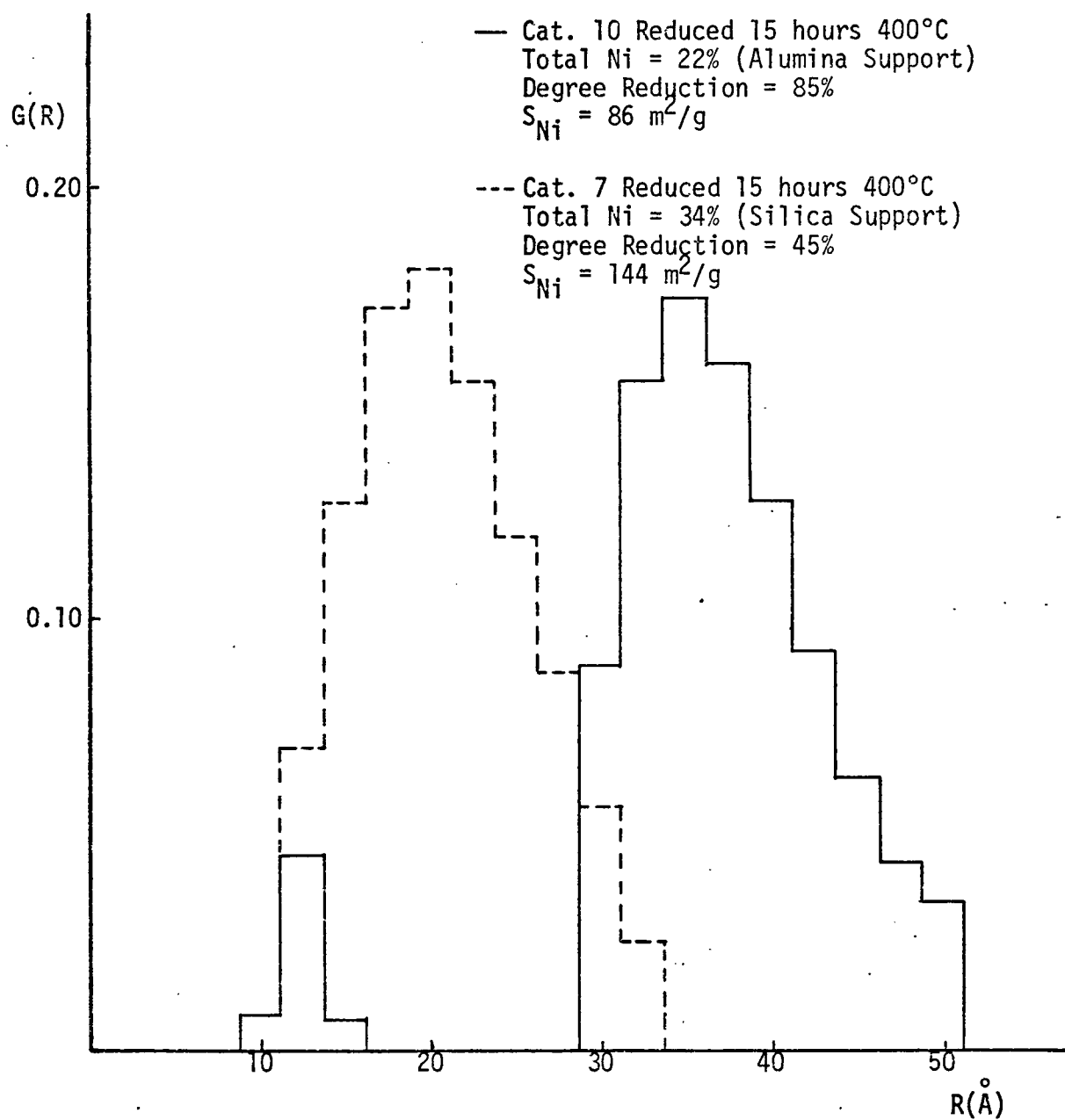


Fig. 8141

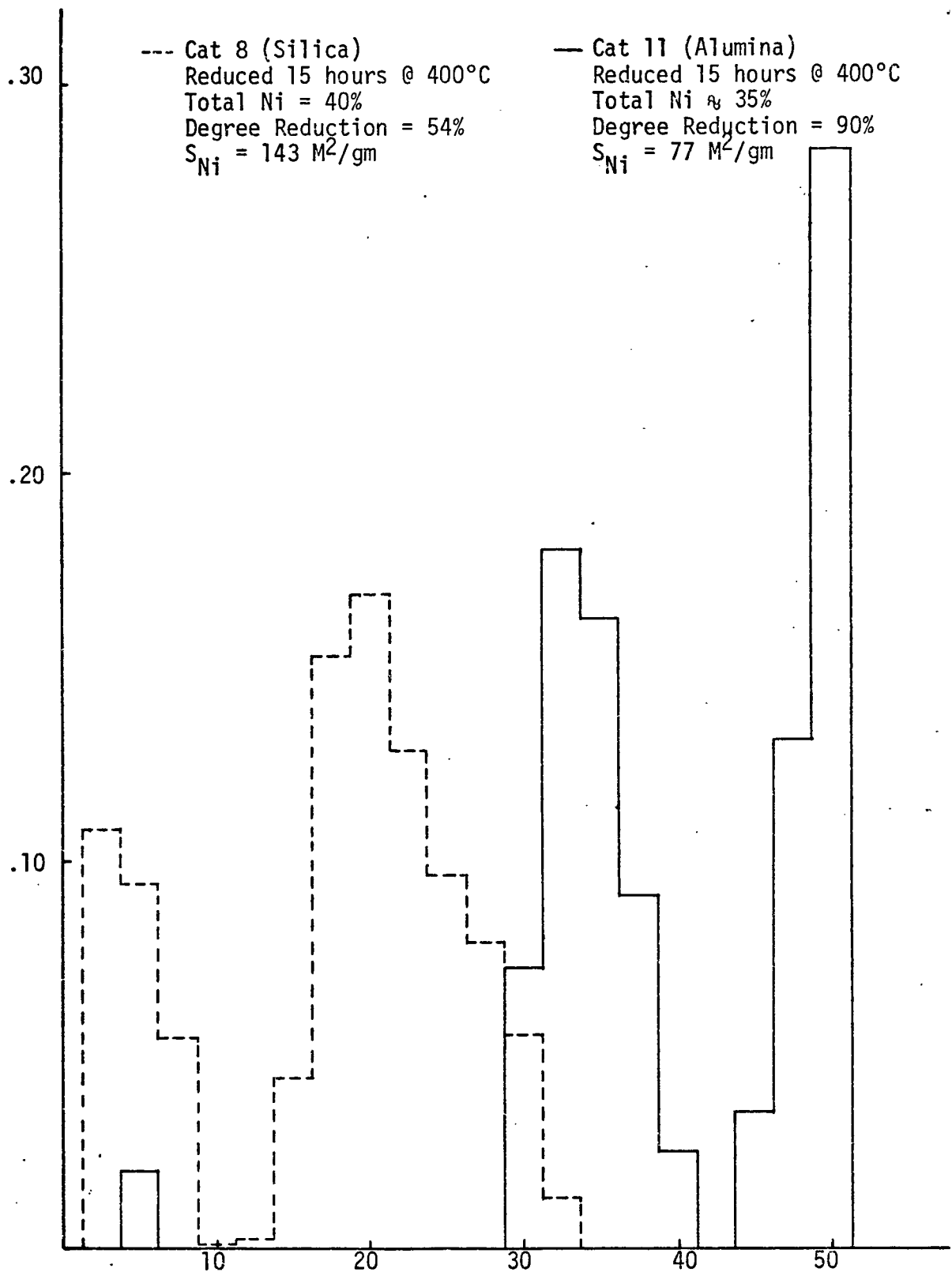


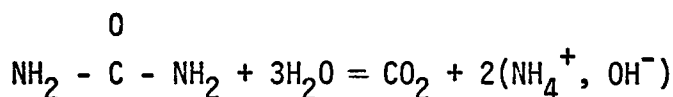
Fig. 8142

and 8142. The alumina supported catalysts exhibit much larger crystallites than the silica-supported ones, although they have a smaller nickel content. Accordingly, the surface areas are almost half of these for the silica catalysts. Finally, it is interesting to note the high degree of reduction of catalysts 10 and 11, compared to the moderate degrees of catalysts 7 and 8. The above observations indicate that the strength of the support-nickel interaction during the precipitation-deposition phase is a critical factor.

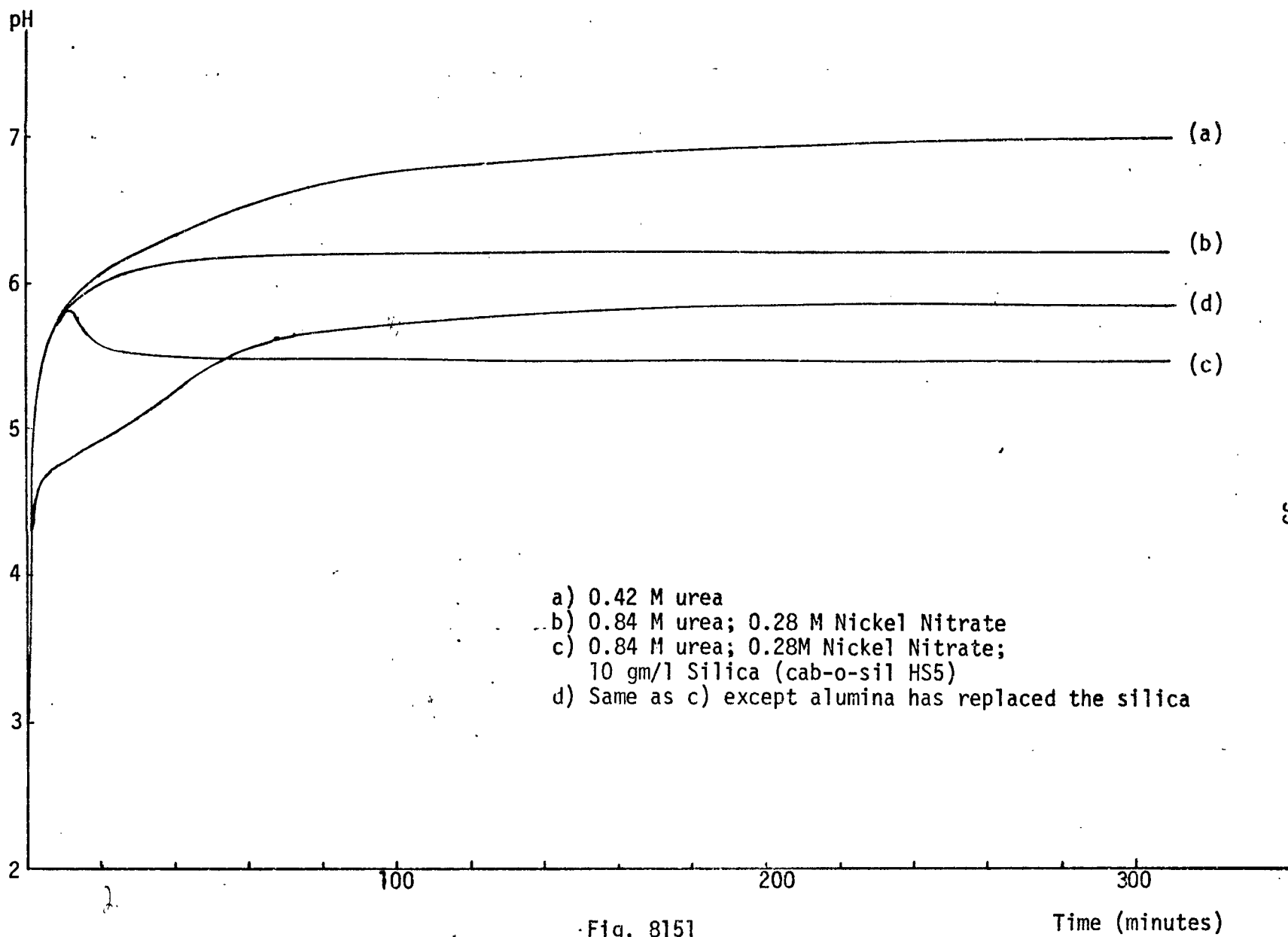
815 Chemistry of the Precipitation-Deposition of Nickel Onto the Support

As mentioned in Section 814, the interaction of the support with the precipitating material is of paramount importance. In this section, a few observations will clarify the mechanism of the preparation.

The thermal decomposition of urea in water at temperatures above about 70°C leads to carbon dioxide and ammonia.⁽²³⁾



Most of the CO₂ dissolved as carbonate ions in the solution. The pH vs. time curve (Fig. 8151, curve a) of 0.42 M urea at 90°C becomes flat after about 5 hours. The final pH is 7.0 which is expected for a weak acid-weak base mixture.



pH - Time Curves for different solutions

When nickel nitrate precipitates in the absence of support, the pH levels off rapidly at a steady value (Fig. 8151, curve b): The rate of production of the hydroxyl ions equals the rate of consumption by the nickel and pH remains unchanged.

With the silica, the precipitation occurs at a lower pH value, showing that precipitation in the bulk of the solution must be rejected. Also the pH vs. time curve displays a transient maximum.

In presence of the alumina (Fig. 8151, curve d), the pH vs. time curve has no maximum. The pH levels off at an intermediate value higher than the value with silica as the support but lower than the value when no support is present.

van Dillen et al⁽²⁾ in their earlier work reported also the existence of a transient maximum of the pH in presence of silica. They also noted that the precipitation pH when silica is used is significantly lower than it is when no support is present. From X-ray diffraction studies and electron micrographs, van Dillen et al⁽²⁾ concluded that the transient maximum in pH observed at 90°C was connected to the formation of a nickel hydrosilicate compound, $\text{Ni}_3(\text{OH})_4 \text{Si}_2\text{O}_5$.

When no support is used, the nickel hydroxide precipitates in the bulk of the solution. The resulting precipitate is a stacking of layered platelet units highly clustered. The interaction within a unit is strong, but small between the composite layers.⁽²⁾ Growth perpendicular to layer will be much slower than growth parallel to the direction of a layer. Since the edges of a layer expose a rather

small area, crystallization will be slow. As a result, the rate of hydroxyl ions generation can keep up with the crystallization rate and the pH levels off.⁽²⁾ If silica is used as the support, the resulting precipitate has the layer structure of nickel hydro-silicate.⁽²⁾ In contrast to unsupported nickel hydroxyl, the formation of hydrosilicate does not remain restricted to the edges of the layers.⁽²⁾ Each layer thickens when a substantial fraction of the silica reacts with penetrating nickel ions. The resulting rate of nucleation of nickel hydrosilicate is fast, especially at higher temperatures.⁽²⁾ Consequently, when urea is added to the solution at 90°C, nucleation of nickel hydrosilicate leads to a fast consumption of hydroxyl ions so that the pH displays a transient decrease. As the pH decreases, the rate of nucleation progressively slows down due to the net consumption of one of the reactants (hydroxyl ions). Then it levels off when the production of hydroxyl ion by urea is maintained.

In the case of alumina, no strong interaction between the precipitating nickel and the support exists and the pH curve has no maximum. The resulting catalyst is much easier to reduce than that prepared with silica (Section 814). The crystallites on alumina are bigger because in the absence of strong support-hydroxide interaction the hydroxide would rather deposit onto an already existing nucleus on the support than an other vacant site of the support. On silica, the strong silica-nickel interaction forces the nuclei to combine intimately with the silica structure, forming uniform

layers of nickel hydrosilicate. Upon reduction, these uniform layers of nickel hydrosilicate generate small crystallites of nickel.⁽²⁾ If the layers are thin, i.e., if the amount of nickel deposited is not too large, they will break during reduction in a uniform manner to yield nickel crystallites uniformly distributed in size. With increasing amounts of nickel, the chances of obtaining a uniform dispersion decrease, and this is observed experimentally (Section 811 and 812).

A last interesting point is that conversion of an appreciable fraction of the silica into a compound having a layer structure has a profound affect on the texture of the support, at least at high nickel-to-silica ratios. This explains why the two most heavily loaded catalysts (catalysts 8 and 9) have a much lighter texture than the other catalysts prepared in the same way. They also are the easiest to reduce, probably because the hydrogen penetrates more easily in the new structure. Catalyst 8 and 9 both contain 40 wt% nickel, although the precipitation time was 8 and 14 hours, respectively. Considering that pure nickel hydrosilicate $\text{Ni}_3(\text{OH})_4\text{Si}_2\text{O}_5$ has 46 wt% nickel, it is possible that all the silica has been consumed after 8 hours to form the silicate. The resulting catalysts would be mainly a hydrosilicate of nickel with 6% moisture and impurities content.

82. Effect of Reduction Conditions

821. Temperature of Reduction

Catalysts 2, 4, 5 and 6 were also reduced at 500°C in hydrogen. Even after only 4 hours reduction, these catalysts sintered significantly. The CSD are given in Fig. 8211 to 8214 along with the CSD of the catalysts reduced at 400°C.

A more severe reduction alters the CSD a great deal on each sample tested. The surface area is lower and bimodal distributions are produced. An increased degree of reduction can be responsible for generating two classes of crystallites: A group of small particles readily reduced at 400°C and a group of larger particles harder to reduce which would appear only at 500°C. Another possible interpretation is sintering by coalescence of particles. A study of sintering effect on the CSD is in progress in this laboratory.⁽²⁴⁾

822. Effect of Reduction Time

The influence of the reduction time on the CSD was checked on catalyst 2. It was reduced at 400°C in flowing hydrogen (80-85 cc/mn) for 5, 10 and 15 hours. The resulting distributions are practically identical (see Figs. 8221 to 8223) and the metallic surface area decays only very slightly with increased reduction time.

The most significant effect is an increased degree of reduction. Thirty percent of the available nickel is reduced after 5 hours, 35%

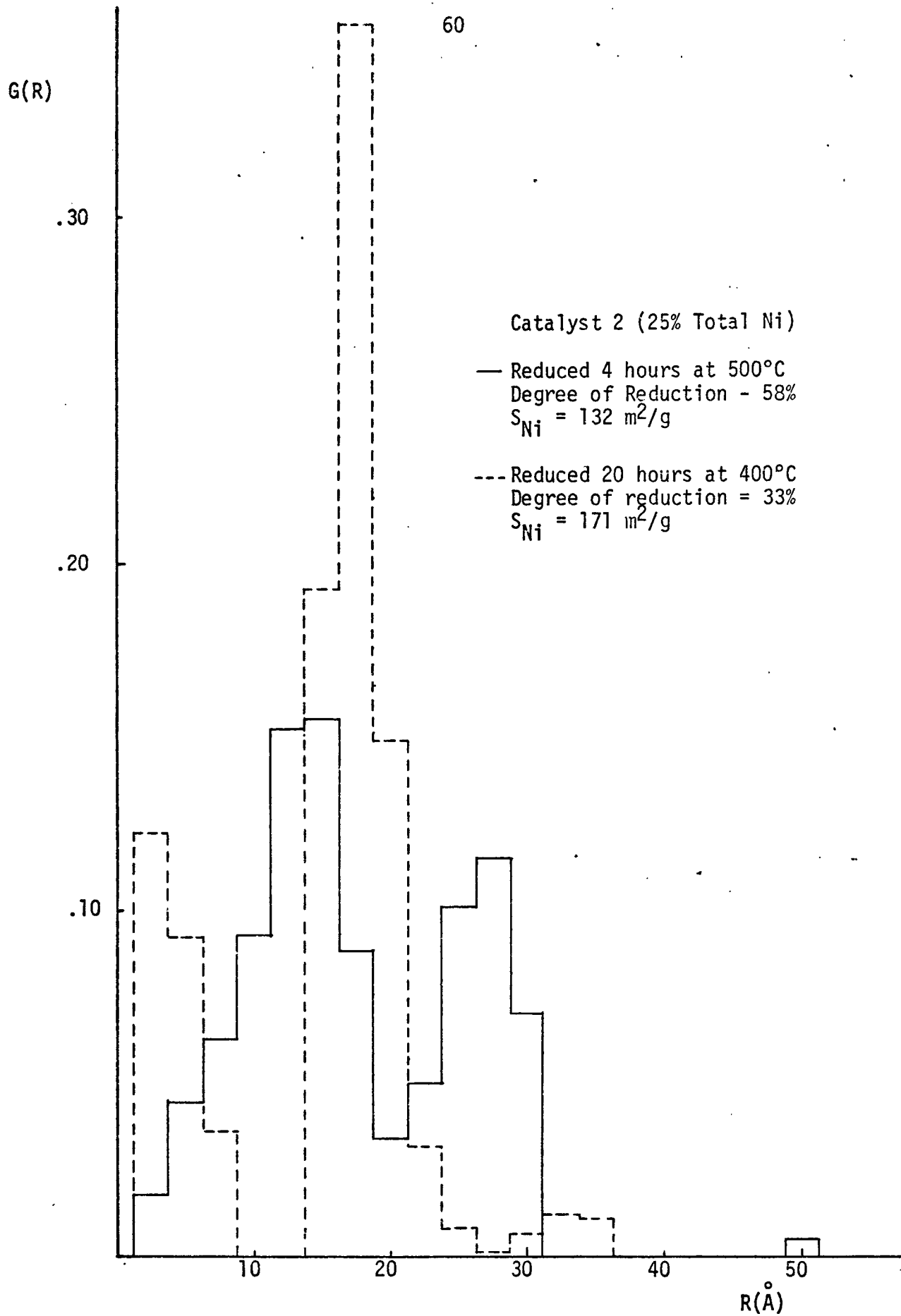


Fig. 8211

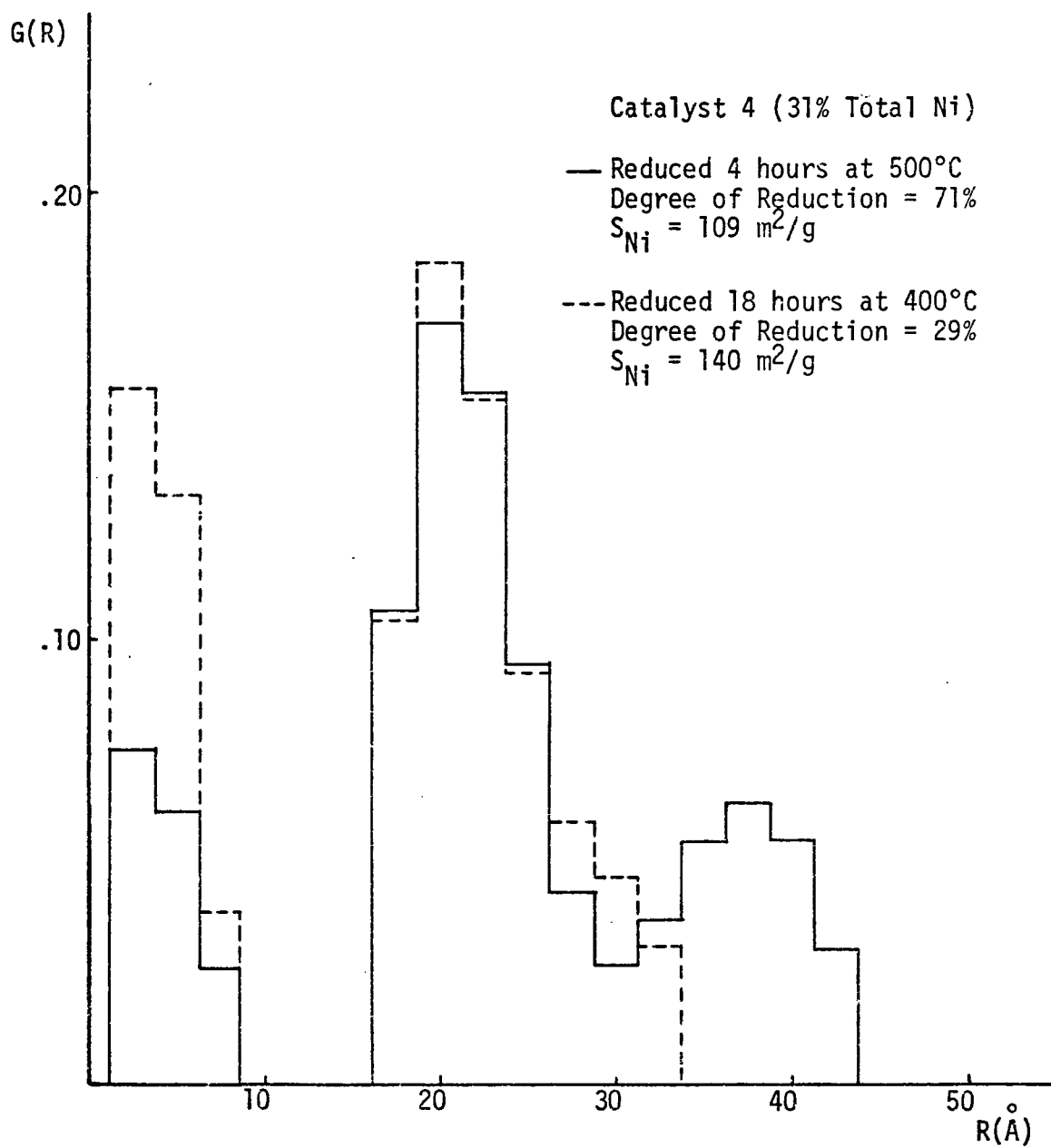


Fig. 8212

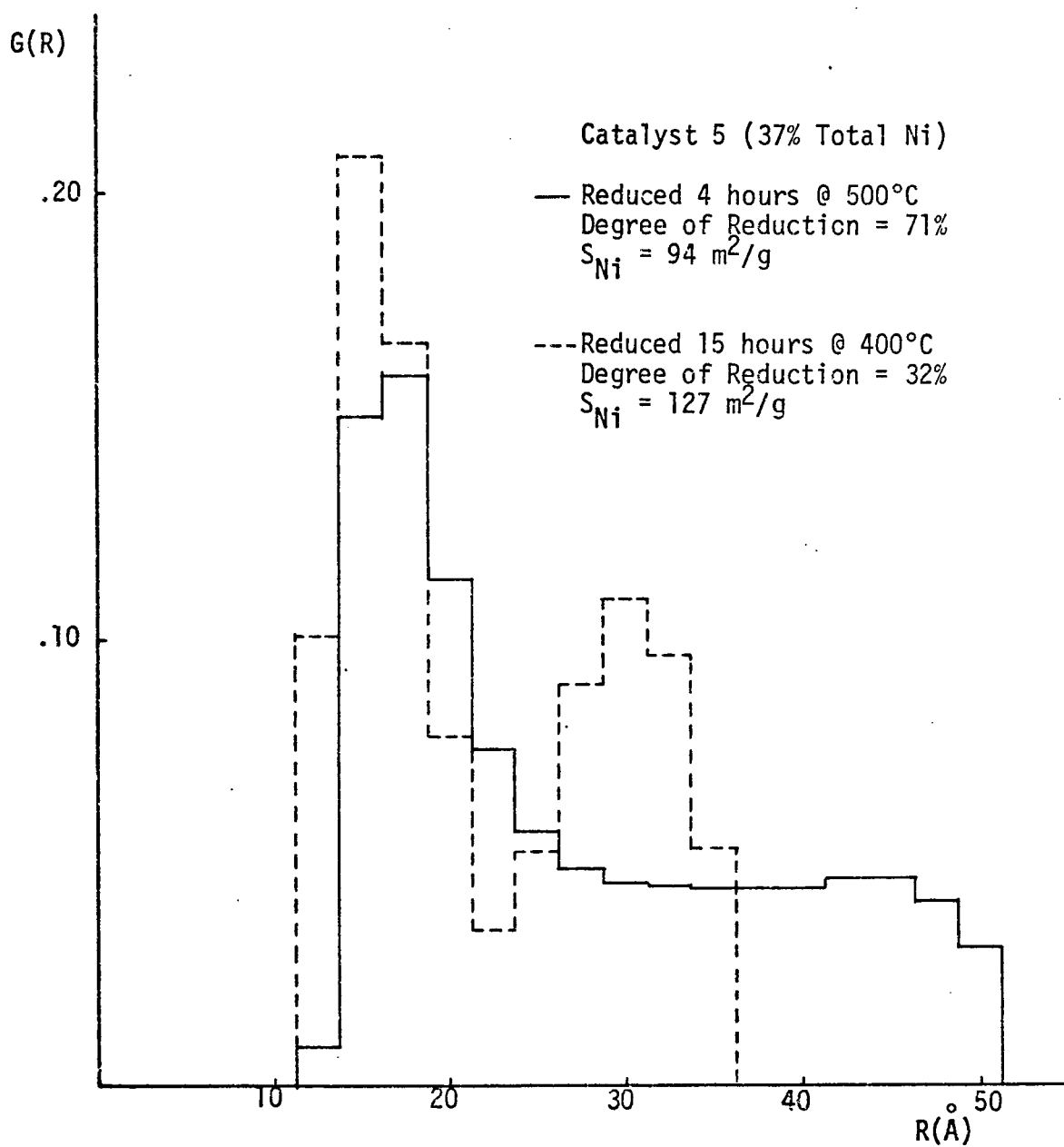


Fig. 8213

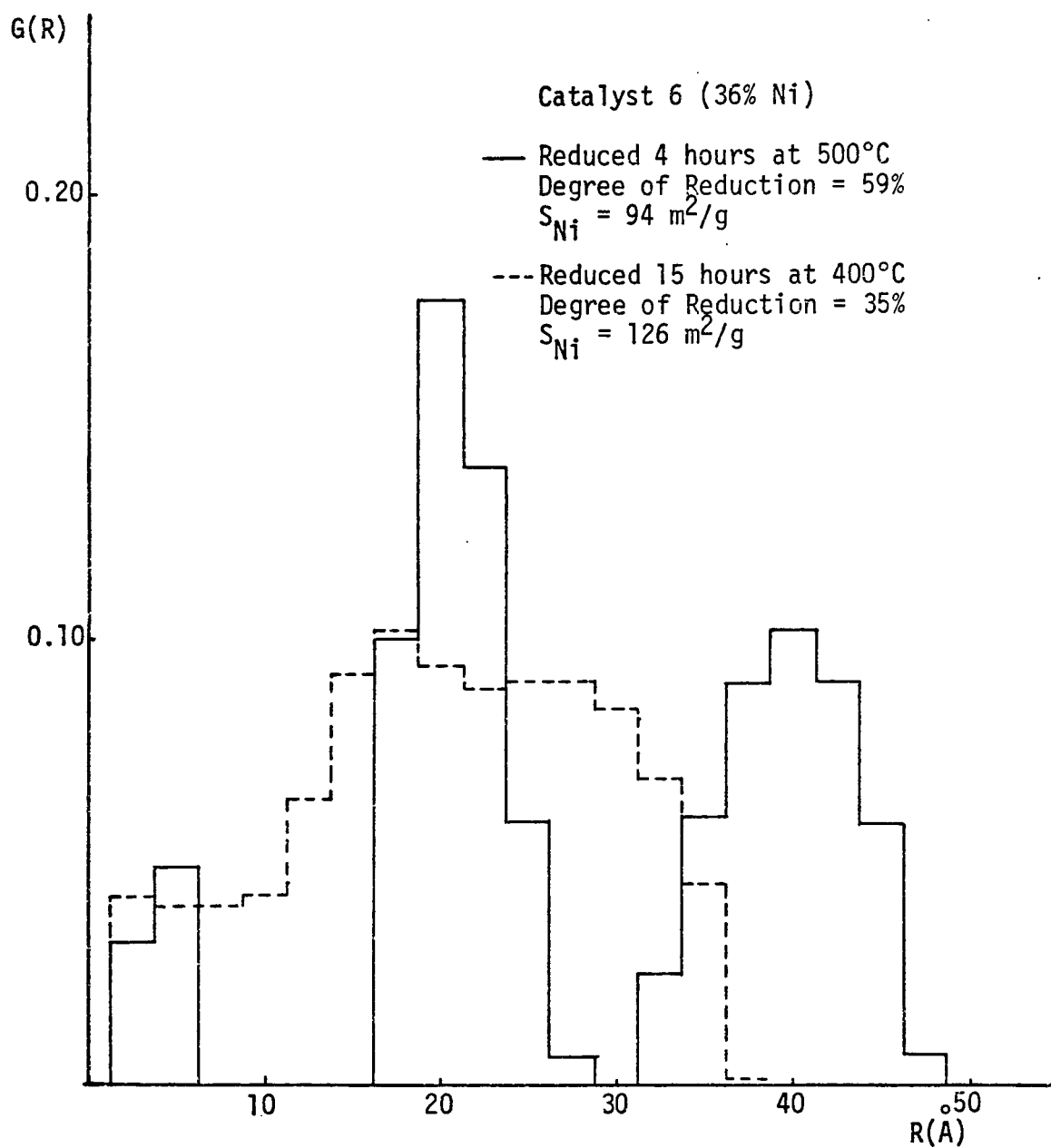


Fig. 8214

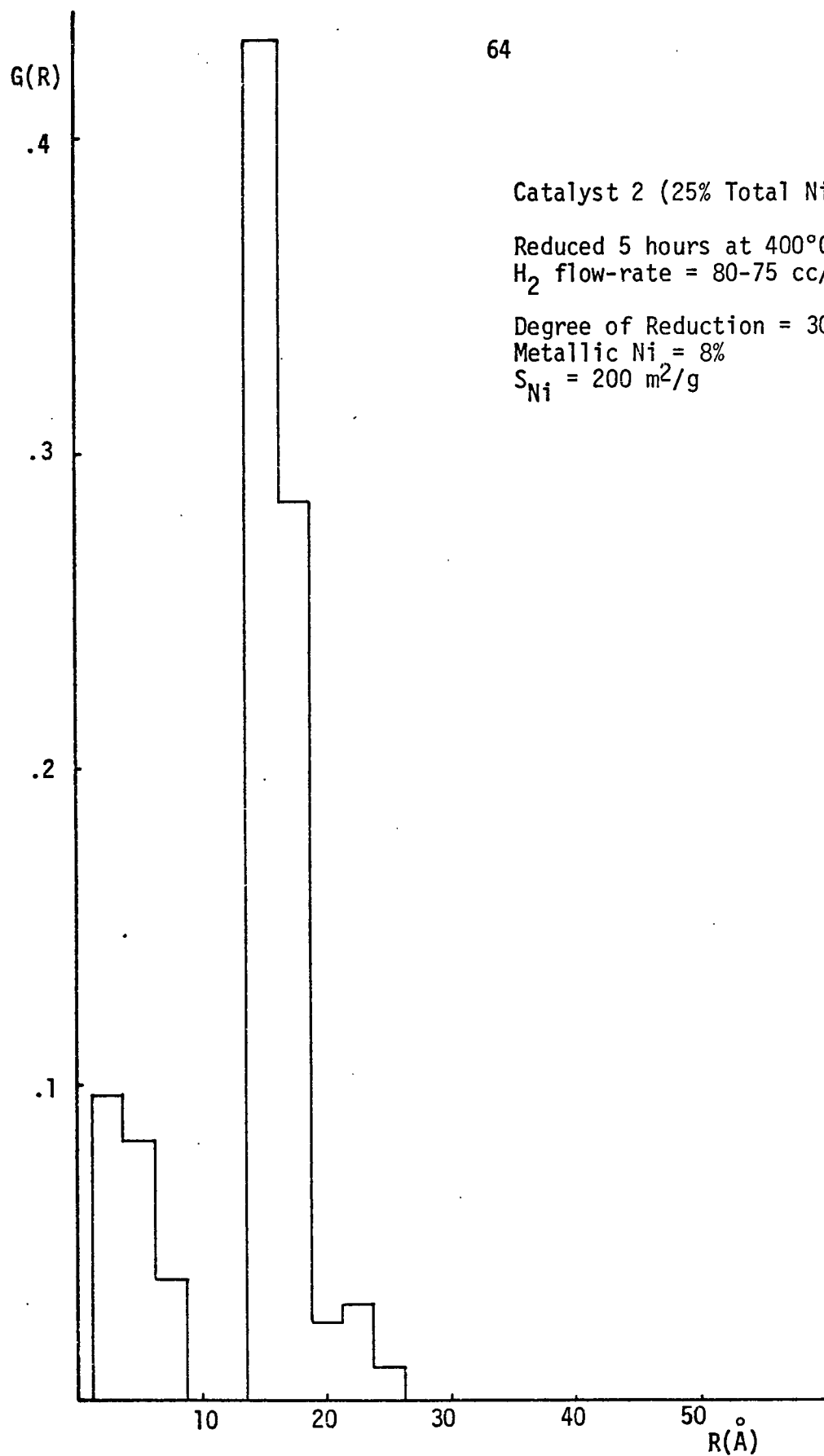


Fig. 8221

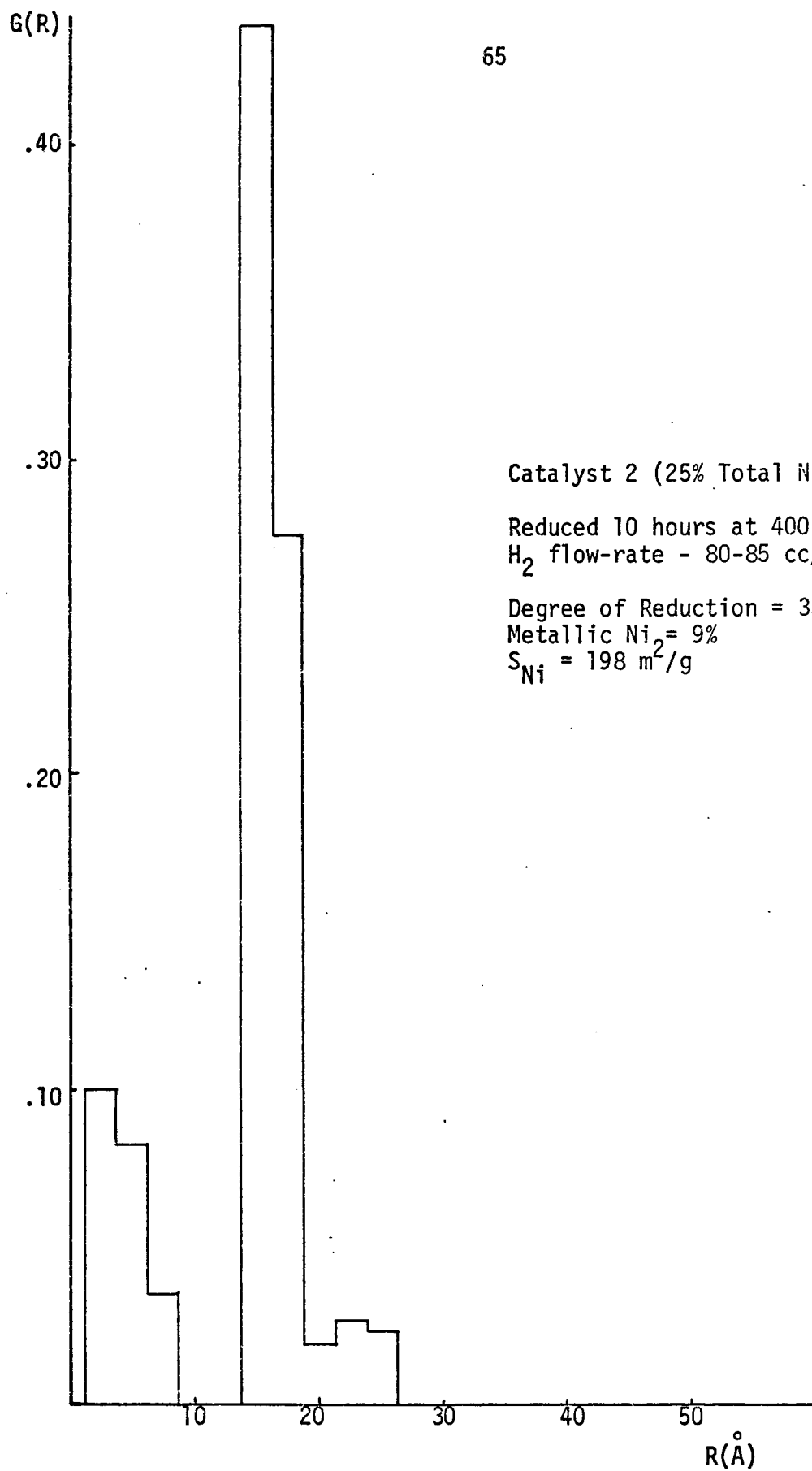


Fig. 8222

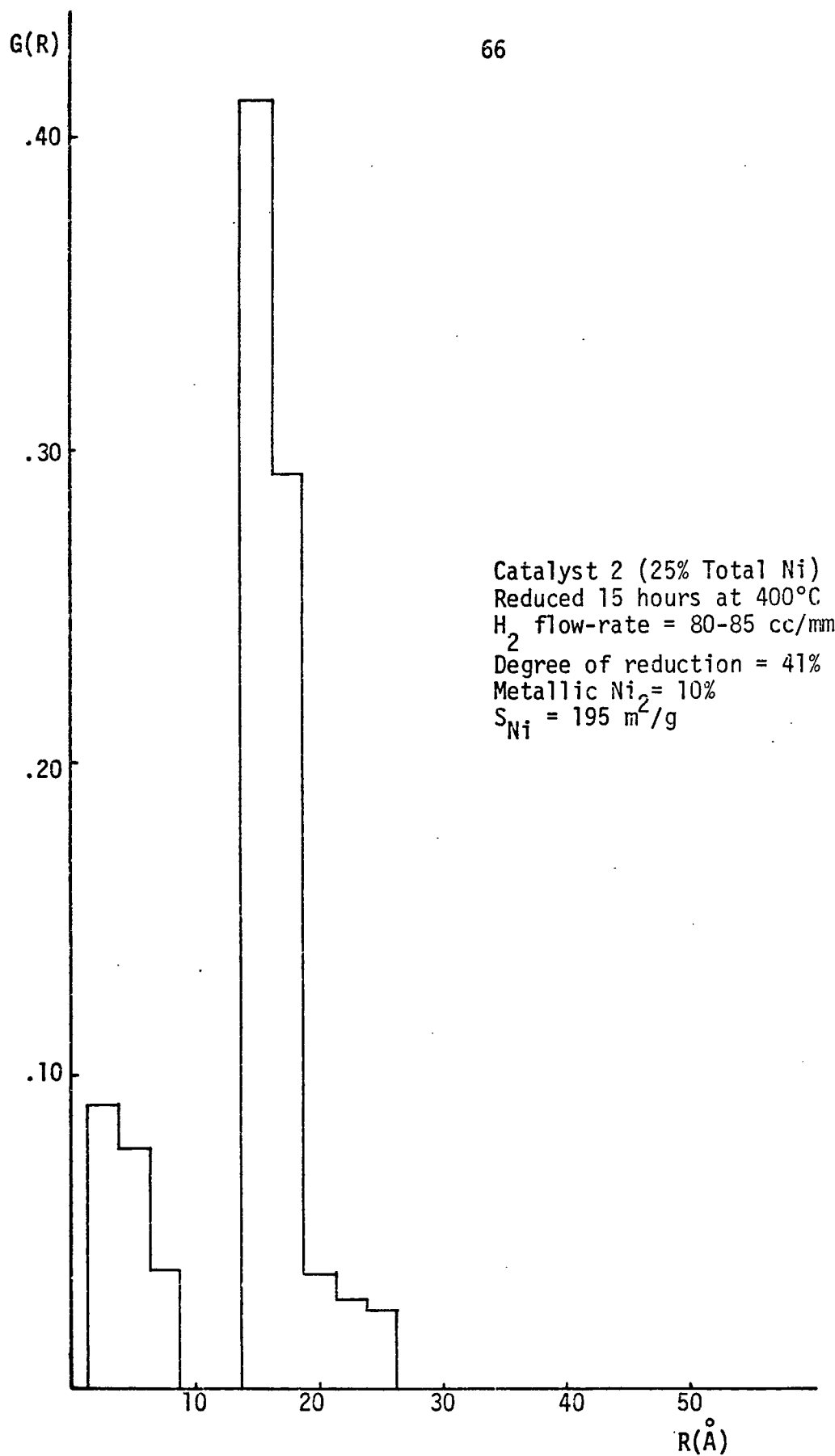


Fig. 8223

after 10 hours, and 41% after 15 hours. The reduction is a slow process after the first initial period. This slow rate of reduction has been reported also for impregnated nickel on silica catalysts.⁽²⁵⁾

823. Hydrogen Flow-Rate

Catalyst 2 (25 wt% nickel) has been reduced using different hydrogen velocities, everything else being the same for that matter.

Upon increasing the hydrogen flow-rate from 20-25 cc/mn to 80-90 cc/mn, the CSD slightly shifts toward smaller particles (Fig. 8231) and roughly keeps its sharp shape. At the same time, more nickel is reduced and the metal surface area increases from 171 M²/gmNi to 201 M²/gmNi. A further increase in flow-rate to 130-150 cc/mn leaves the CSD and the nickel surface area unchanged but still improves the degree of reduction (Fig. 8232).

High hydrogen flow-rate is then much favorable in improving the dispersion and producing more nickel available per gram of catalyst. These effects were also observed on two other catalysts much different from each other (Fig. 8233 and 8234).

The significantly improved degree of reduction upon increased flow-rate indicates a mass transfer-controlled situation or a better gas distribution in the rather compact catalyst bed.

The Reynolds number for the flow through an annulus is:

$$Re = 2(R-r) v \rho/\mu$$

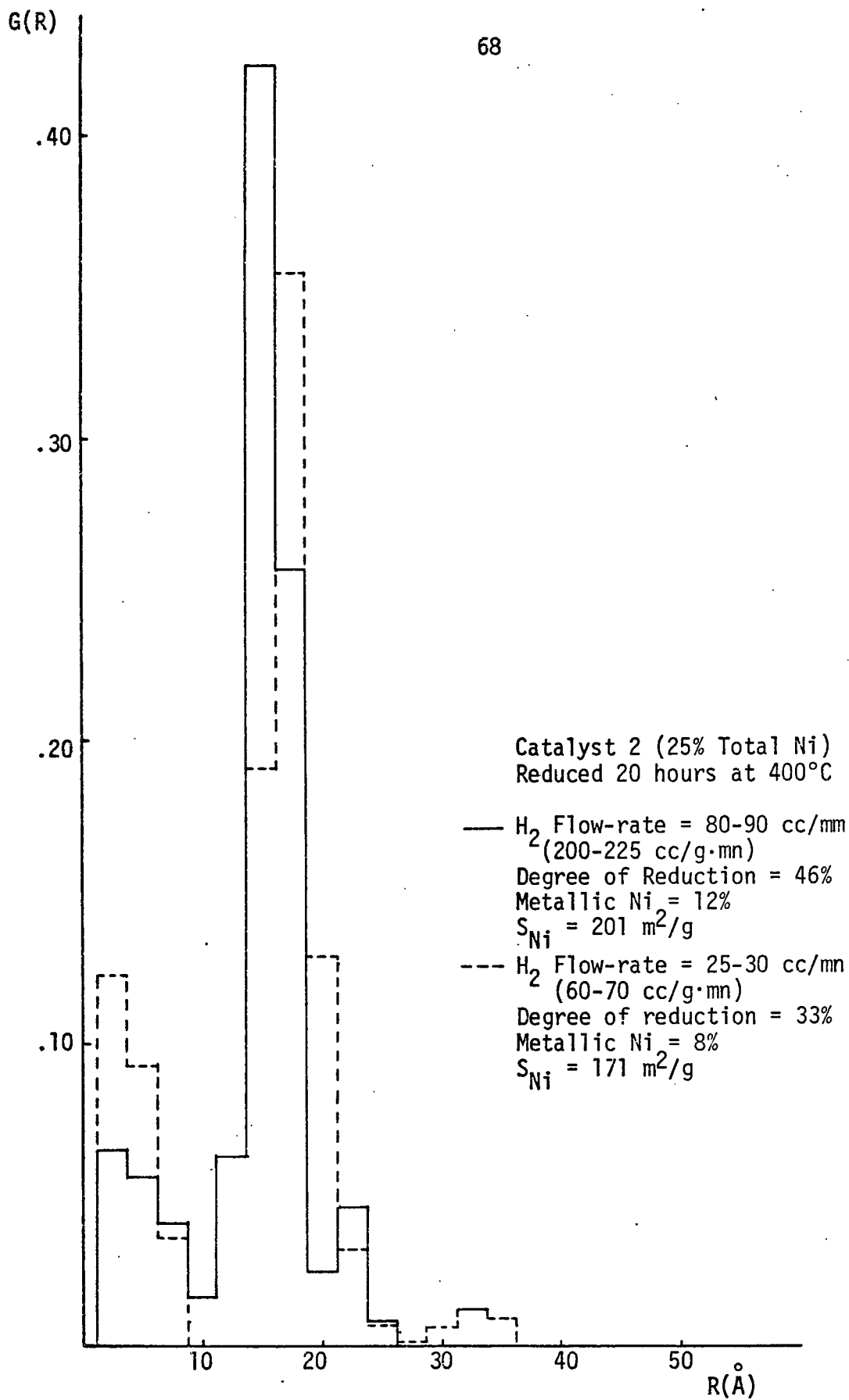


Fig. 8231

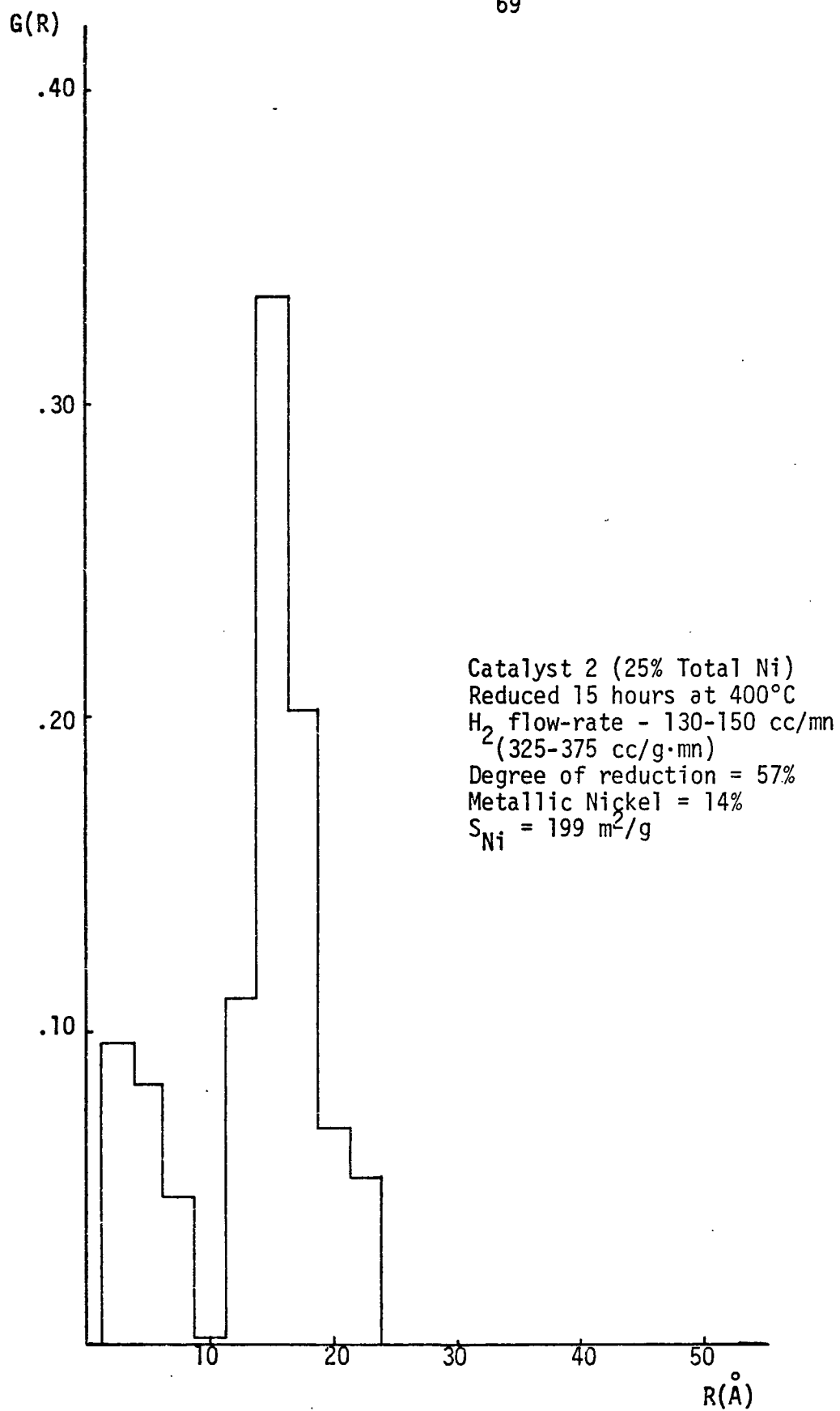


Fig. 8232

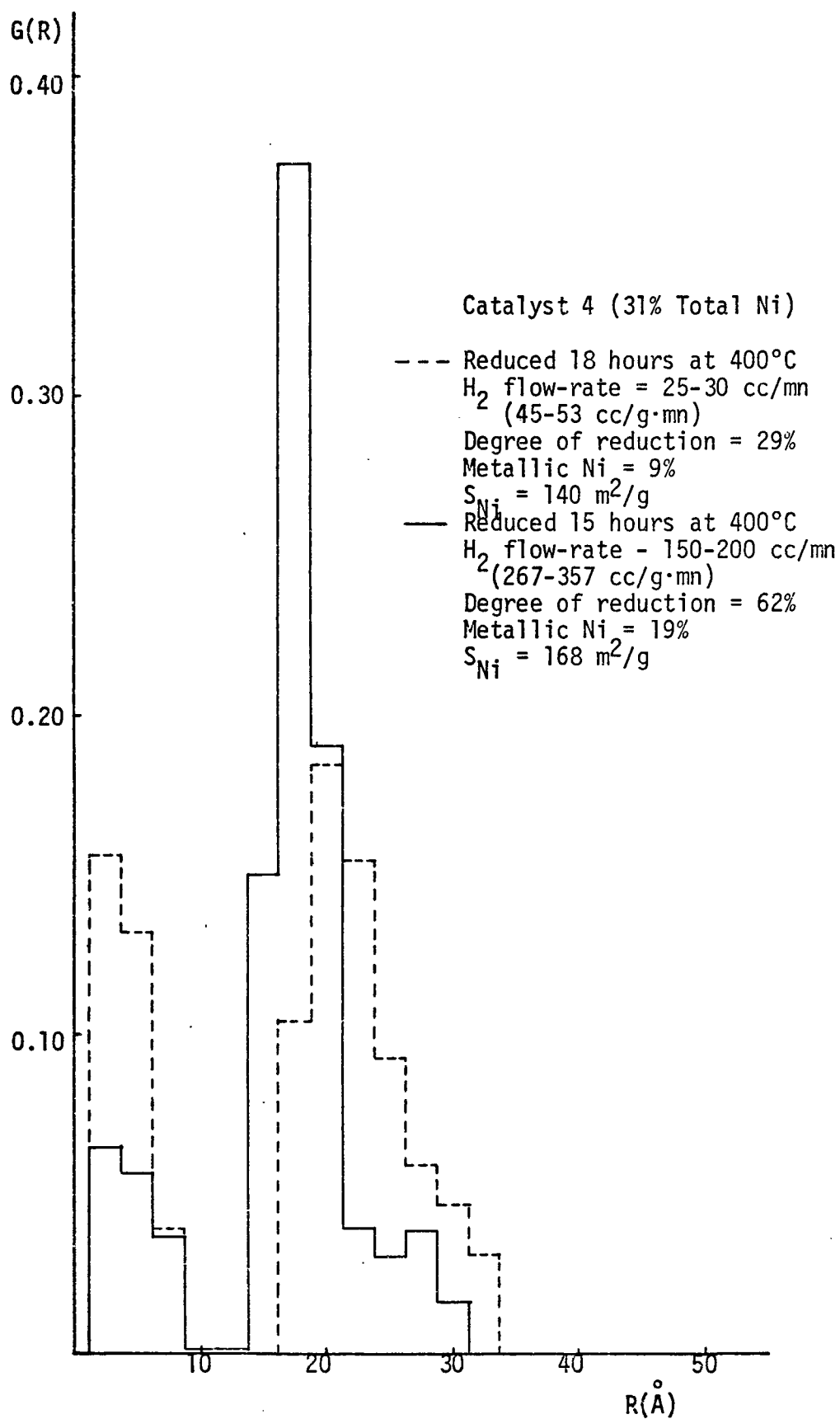
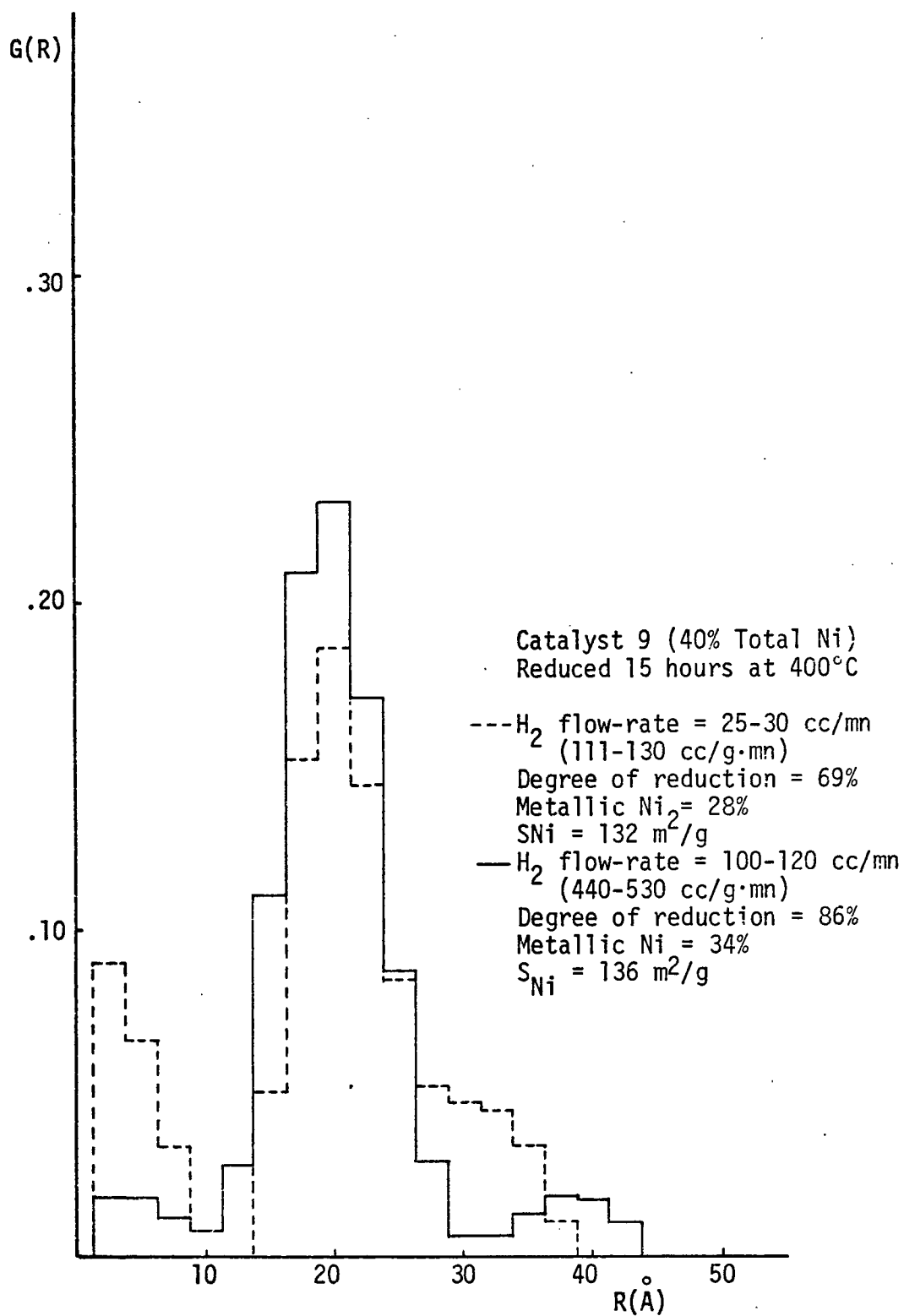


Fig. 8233



The sample cell used is a cylindrical annulus with radii $R = 0.5$ cm and $r = 0.15$ cm. The density of hydrogen at 400°C is about

$$\rho = 3.6 \times 10^{-5} \text{ g/cm}^3$$

The viscosity at 400°C estimated empirically from the critical data is

$$\mu = 105 \times 10^{-6} \text{ poise for hydrogen}$$

The cross-sectional area of the annulus is about 0.70 cm^2 . A flow of $30 \text{ cm}^3/\text{mn}$ gives a velocity v equal to about 0.7 cm/sec . The Reynolds number becomes

$$\text{Re} = \frac{2(0.5 - 0.15) \times 0.7 \times 3.6 \times 10^{-5}}{105 \times 10^{-6}}$$

$$\text{Re} = 0.17 \text{ at } 400^{\circ}\text{C} \text{ and } 30 \text{ cm}^3/\text{mn}$$

The transition laminar to turbulent for a flow through an annulus occurs at $\text{Re} \approx 2000$. Even at $200 \text{ cm}^3/\text{mn}$, the flow is well in the laminar region.

Increased surface area and more uniform CSD with higher hydrogen velocities are likely the results of two effects: (i) More effective transport of water from the sample at higher space velocities and (ii) More effective removal of heat generated by exothermic reduction at higher flow-rates, thus minimizing temperature excursions and hot spots in the catalyst.

Bartholomew⁽²⁶⁾ recently reported identical effects of hydrogen velocity during reduction of nickel on alumina catalysts prepared by impregnation. It was also found that nickel surface area and the fraction of nickel reduced to the metallic state both increased as the hydrogen space velocity during reduction was increased.

83. Effect of Calcination

Prior to reduction, catalyst 2 was calcined at 350°C in dry air for two hours (air flow-rate = 100-120 cc/min). Then it was reduced at 400°C in hydrogen for 15 hours (H_2 flow-rate = 25-30 cc/min).

Fig. 83 compares the CSD of the calcined catalyst with the CSD of the catalyst reduced directly.

Considering the relatively poor accuracy of the magnetization data (due to low nickel content in the sample_ the differences observed in the CSD's, surface area and degree of reduction are not significant. It is safe to say however that calcination did not affect the catalyst very much.

A calcination treatment at 450°C in the same conditions did not bring any significant change in the magnetization data.

Calcination sometimes results in poorer reducibility and lower surface area.⁽²⁶⁾ The last effect is ascribed to sintering due to the large heat of oxidation of nickel. In our case, the high air flow-rate might have prevented the latter effect by enhancing heat dissipation.

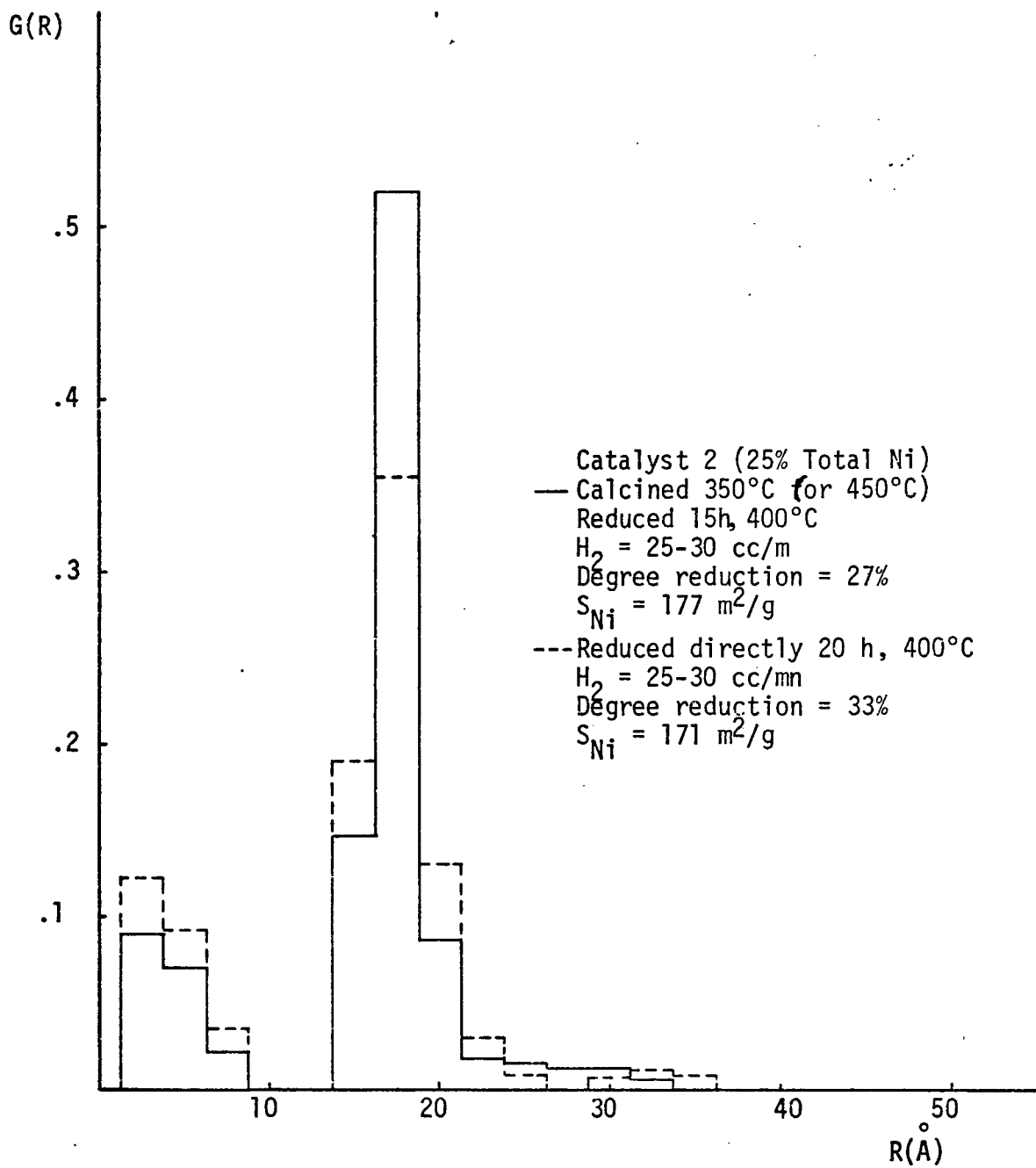


Fig. 83

84. Effect of Adsorbed Hydrogen and Oxygen on the Magnetization of a Reduced Catalyst

It was of interest to investigate the influence of chemisorbed hydrogen which is known to lower the magnetization of finely dispersed nickel catalysts.⁽²⁰⁾ Such an effect could invalidate the data if care were not taken to remove any adsorbed gases. (The effect is not limited to hydrogen: it is present whenever chemisorption occurs). That is why the catalysts were cleaned in argon after reduction as described in Section 7.

To see the extent of this effect, an adsorption of hydrogen/cleaning in argon sequence was conducted on catalyst 4. This catalyst is highly dispersed after reduction at 400°C and is therefore a good test sample. Some catalyst (1,2) had even smaller crystallites but as a result had a poorer magnetic response.

The sequence of treatment was the following:

1. The catalyst was reduced at 400°C for 15 hours in a flow of hydrogen (Flow-rate = 150-200 cc/mn), the catalyst was cooled to room temperature in hydrogen atmosphere and the magnetization measured (Fig. 841, curve (1)).

2. The sample was next cleaned in argon at 425°C for one hour. On Fig. 841, curve (2) is the magnetization curve of the cleaned sample. The clean sample has a markedly higher magnetization than the sample saturated with the reduction hydrogen. Cleaning the sample is of prime importance for magnetic measurements.

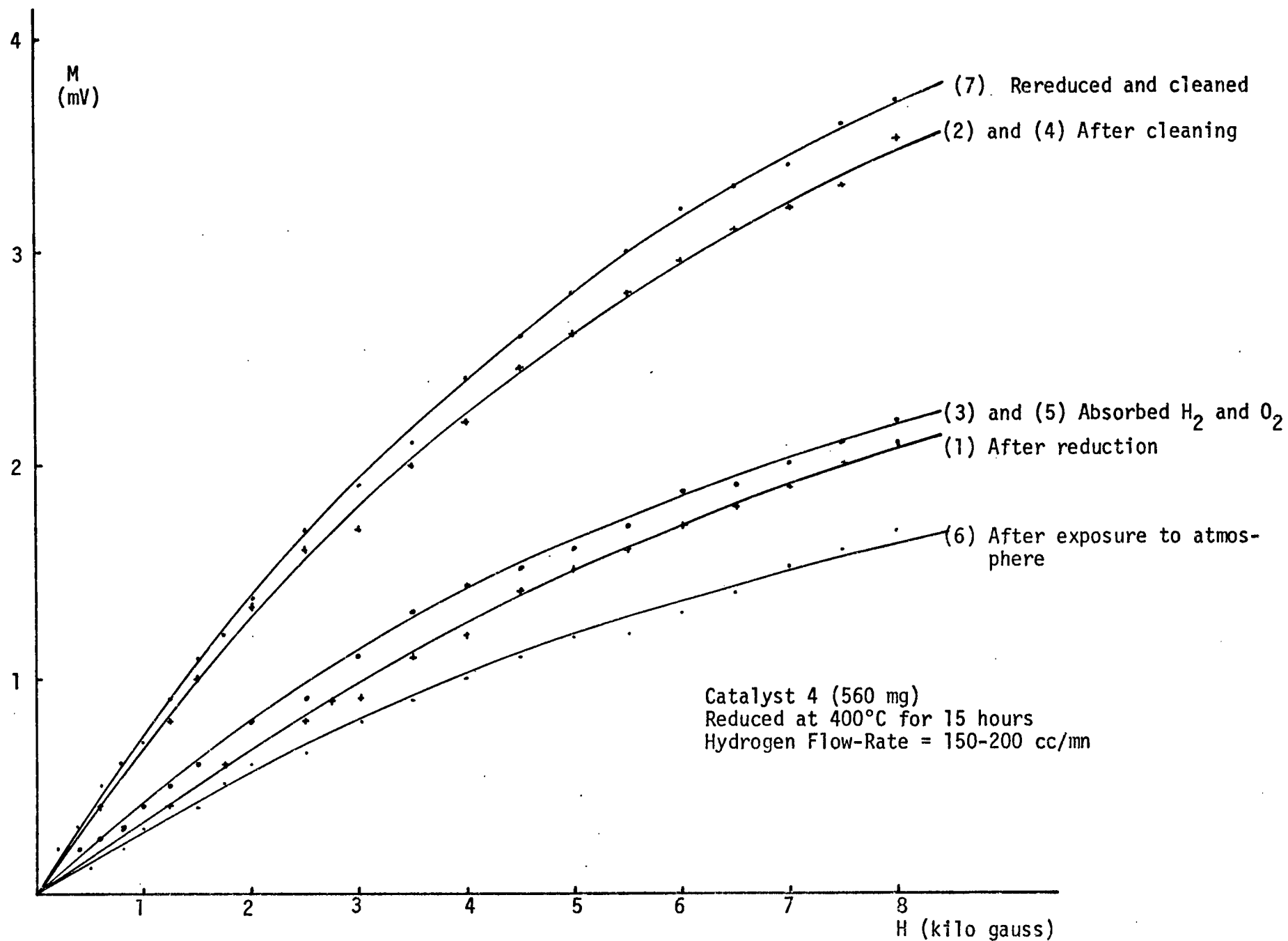


Fig. 841

3. Pure hydrogen was passed on the catalyst for one hour at room temperature. The resulting magnetization curve (curve 3) is almost identical to curve 1. The hydrogen adsorbed at room temperature has an effect comparable to the reduction hydrogen.

4. The hydrogen adsorbed at room temperature in step 3 is out-gassed by flowing argon at 300°C for one hour over the sample. The magnetization curve (curve 4) increases exactly to that of step 2. The cleaning procedures in argon is then effective and reproducible. The adsorption of oxygen on nickel is even stronger than that of hydrogen. The heat of adsorption for oxygen is about three times higher than it is for hydrogen. One may then wonder what the effect of adsorbed oxygen is on the magnetization, and whether the oxygen can be removed by reduction without affecting the catalyst. A test was performed on the clean sample obtained in step 4 as follows:

5. A mixture of air and argon was passed on the catalyst for one hour at room temperature (2 cc/mn air and 106 cc/mn argon for the first half-hour--6cc/mn air and 106 cc/mn argon for the second half-hour). The adsorbed oxygen had the same effect as the hydrogen for the magnetization curve (5) superposes with curve (3) obtained after hydrogen had been passed onto the sample.

6. The mild oxidation performed in step 5 is a common way of passivating nickel catalysts. To see if the passivation was efficient, the sample cell was left opened to the atmosphere overnight. After overnight exposure, a further drop in magnetization (curve 6) showed

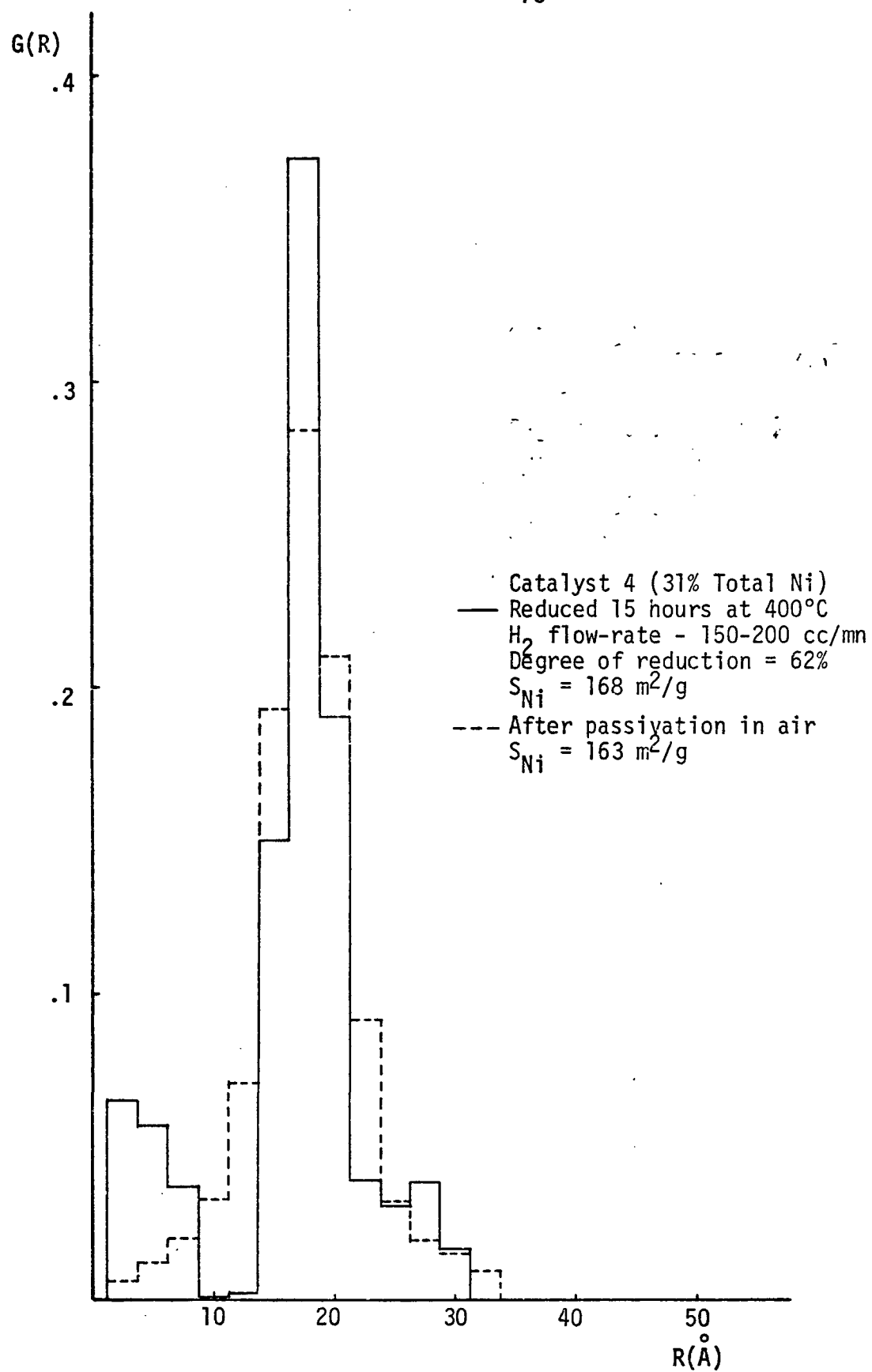


Fig. 842

that further surface oxidation took place. The procedure described in step 5 would be insufficient to protect the catalyst from the atmosphere oxygen.

7. Next the catalyst is rereduced at 350°C in hydrogen for two hours, in order to reduce the oxide layer(s), and finally cleaned in argon at 400°C for one hour. The magnetization curve 7 is slightly above curve 2 or 4. This increase cannot be ascribed to a larger amount of nickel being reduced since 350°C is far below the original reduction temperature. Passivation of the catalyst appears to have increased the magnetization slightly.

At the end of this sequence of treatments, the catalyst was sintered in the usual way to determine the saturation magnetization. Curves 2 and 7 were used as magnetization data to calculate the CSD before and after passivation. The two distributions are very similar (Fig. 842) and the passivation has hardly (if any) disturbed the particle sizes.

Another passivation test confirmed the above results. Fig. 843 shows the magnetization of catalyst 9 after: (1) reduction at 400°C and cleaning in argon at 425°C; (2) passivation by oxygen-argon mixture as done earlier on catalyst 3; (3) rereduction at 350°C for a short time.

The CSD (Fig. 844) before and after passivation are also very close to each other (and so are the surface areas).

Once the catalyst 9 had been sintered, passing pure dry air over it did not visibly affect the magnetization. The sample cell containing

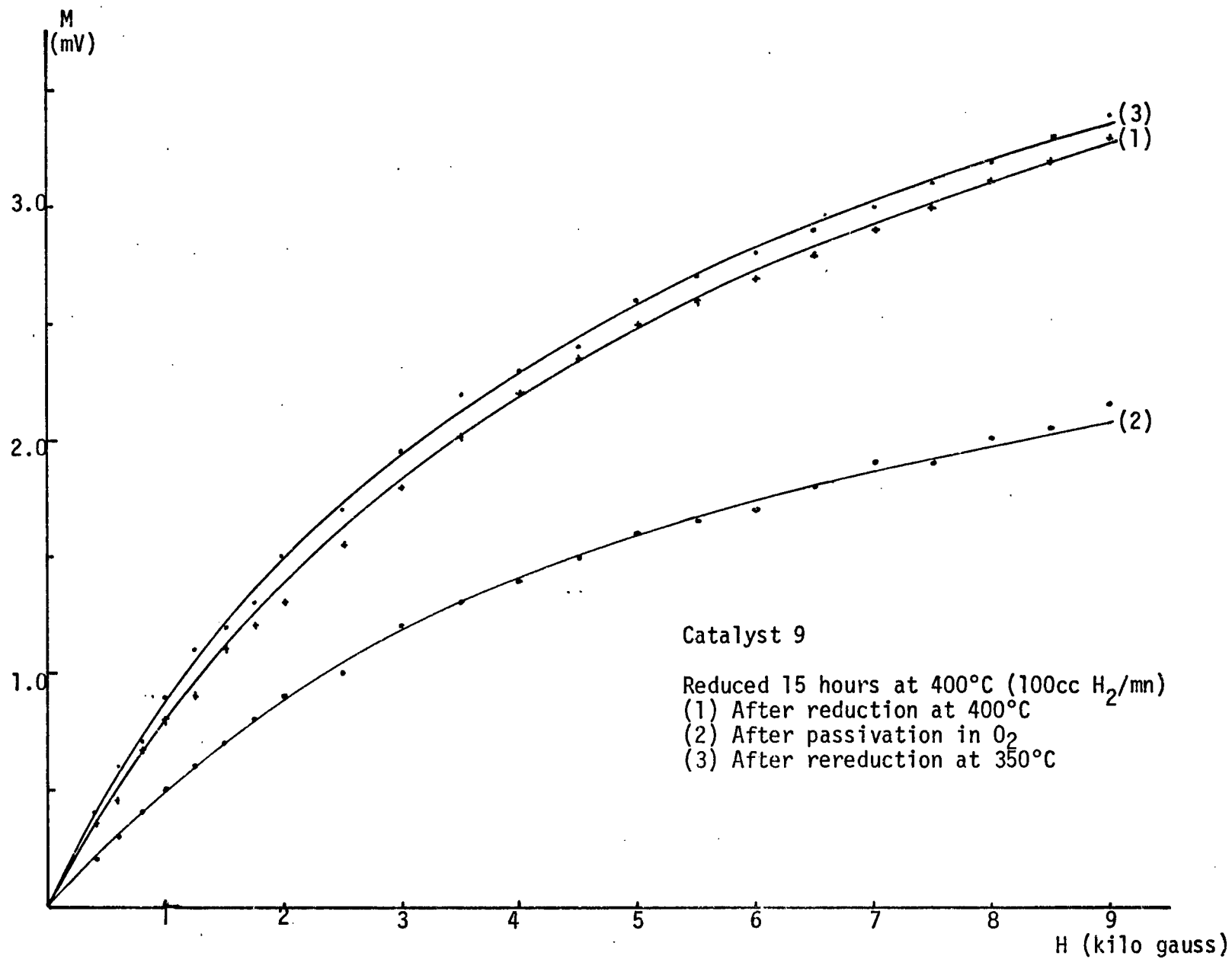


Fig. 843

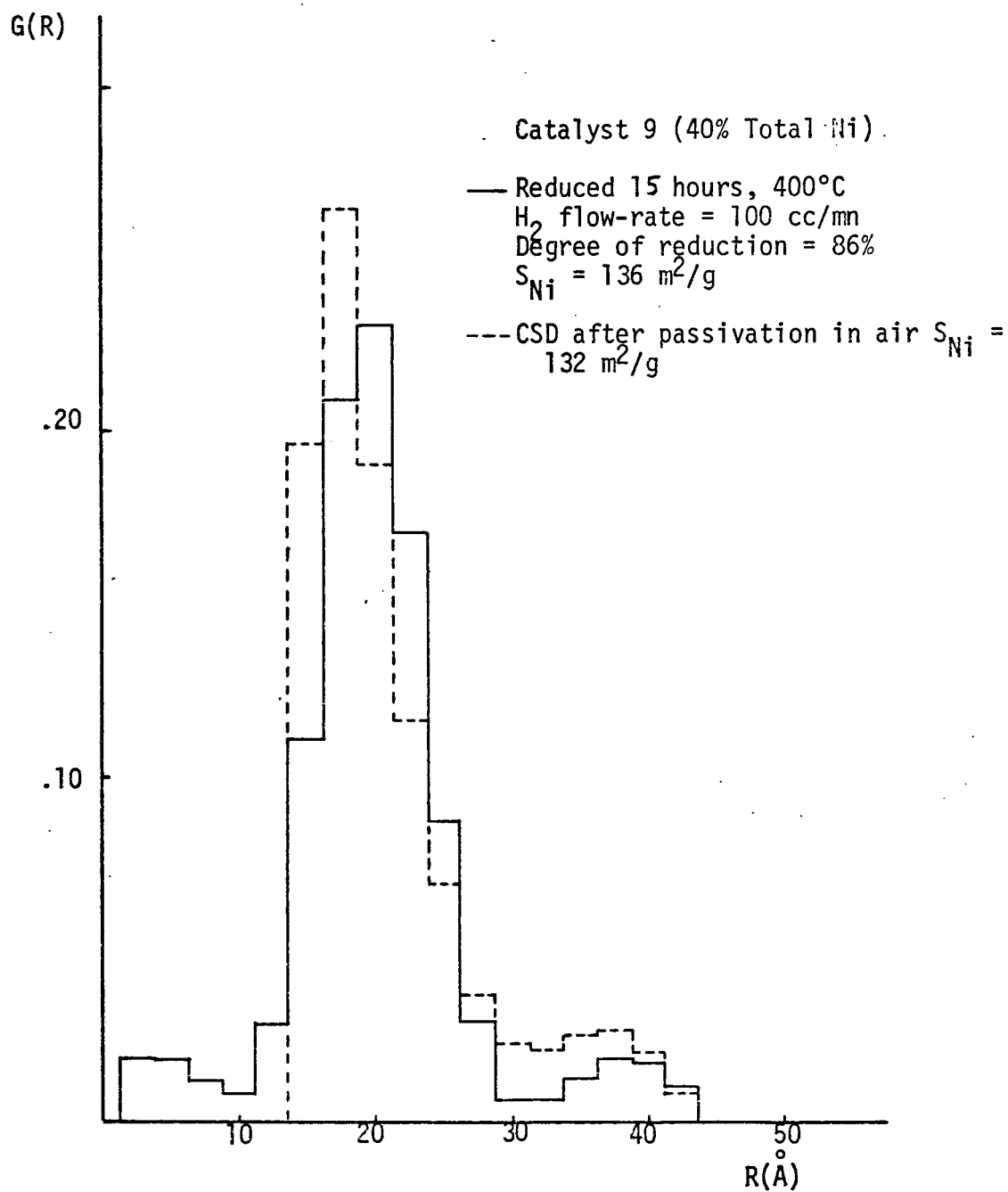


Fig. 844

the sintered sample was left a few days open to the atmosphere and no noticeable change in magnetization occurred whatsoever. This confirmed the interpretation of Selwood⁽²⁰⁾ concerning the decrease in magnetization when species chemisorb at the surface of small superparamagnetic particles. The relative portion of atoms or molecules at the surface of very small particles is large. Upon bonding with chemisorbed species, these atoms lose their unpaired electrons responsible for their paramagnetism. The result is a significant decrease of magnetization on the macroscopic scale. A sintered sample contains big particles in which the relative number of surface atoms is very small.

Selwood⁽²⁰⁾ introduced a quantity ϵ to designate the change in magnetic moment of a nickel particle caused by the adsorption of one atom of hydrogen. A sample containing $n(\text{Ni})$ moles of nickel adsorbing $n(\text{H})$ moles of hydrogen atoms will exhibit a fractional change in the saturation magnetization M_0 (at 0°K) given by:

$$\frac{\Delta M_0}{M_0} = \frac{-\epsilon \times n(\text{H})}{n(\text{Ni}) \times \beta(\text{Ni})}$$

Applying this formula to catalyst 4, the relative change in magnetization observed between curves 2 and 3 on Fig. 841 is about -0.36 (it varies slightly with the applied field). Taking this value as $\frac{\Delta M_0}{M_0}$ we can now calculate $n(\text{H})$.

Selwood reported a value for ϵ of -0.72 from a limited number of data. Our sample had 108 mg of nickel.

$$n(H) = \frac{\Delta M_0}{M_0} \times \frac{n(Ni) \times \beta(Ni)}{\epsilon}$$

$\beta(Ni)$ is the magnetic moment of a nickel atom expressed in Bohr magneton. We will take $\beta(Ni) = 0.606$ following Selwood. Then:

$$n(H) = \frac{-0.36 \times 0.108 \text{ g} \times 0.606}{58.71 \text{ g mole}^{-1} \times (-0.72)}$$

$$n(H) = 5.572 \times 10^{-4} \text{ moles of H}$$

A generally accepted value for the area occupied by one nickel atom is⁽¹⁸⁾

$$6.5 \times 10^{-20} \text{ m}^2/\text{Ni atom}$$

The metallic surface area calculated using $n(H)$ will be, since one atom of H occupies one Ni:

$$S = \frac{5.572 \times 10^{-4} \times 6.02 \times 10^{23} \times 6.5 \times 10^{-20}}{0.108}$$

$$S = 202 \text{ m}^2/\text{g Ni}$$

The metallic surface area calculated from the crystallite size distribution was $168 \text{ m}^2/\text{g Ni}$. Considering the uncertainties involved

in Selwood's formula and the assumptions made in the calculation above, the values obtained are very reasonable.

85. Reproducibility of the Preparation Method Comparison with an Impregnated Sample

There are two main features in the preparation method investigated in this work. The first is the production of catalysts with very uniformly dispersed crystallites of nickel. The second is the reproducibility of the method due to easily controlled preparation parameters.

In the preceding sections, enough evidence of the first feature has been shown, along with some limitations imposed by the preparation and treatment variables. To assess the second feature, two batches of catalysts were prepared independently in the same way. These catalysts are catalyst 2 and catalyst 3. After reduction at 400°C for 15 hours in a flow of hydrogen (80-85 cc/mn), they displayed very similar CSD's as seen in Fig. 851. Their surface areas are very close, and the degree of reduction is identical. The total nickel content in weight per cent differ slightly but this is probably due to different moisture content after drying. The drying operation of these catalysts was not carefully monitored in time and temperature as the drying step is not a critical variable.

The reproducibility of the method is then clearly confirmed by this comparative test. Note that the catalysts 2 and 3 were made by two different operators. One of them had never made a catalyst and just followed the "recipe" given in Section 4.

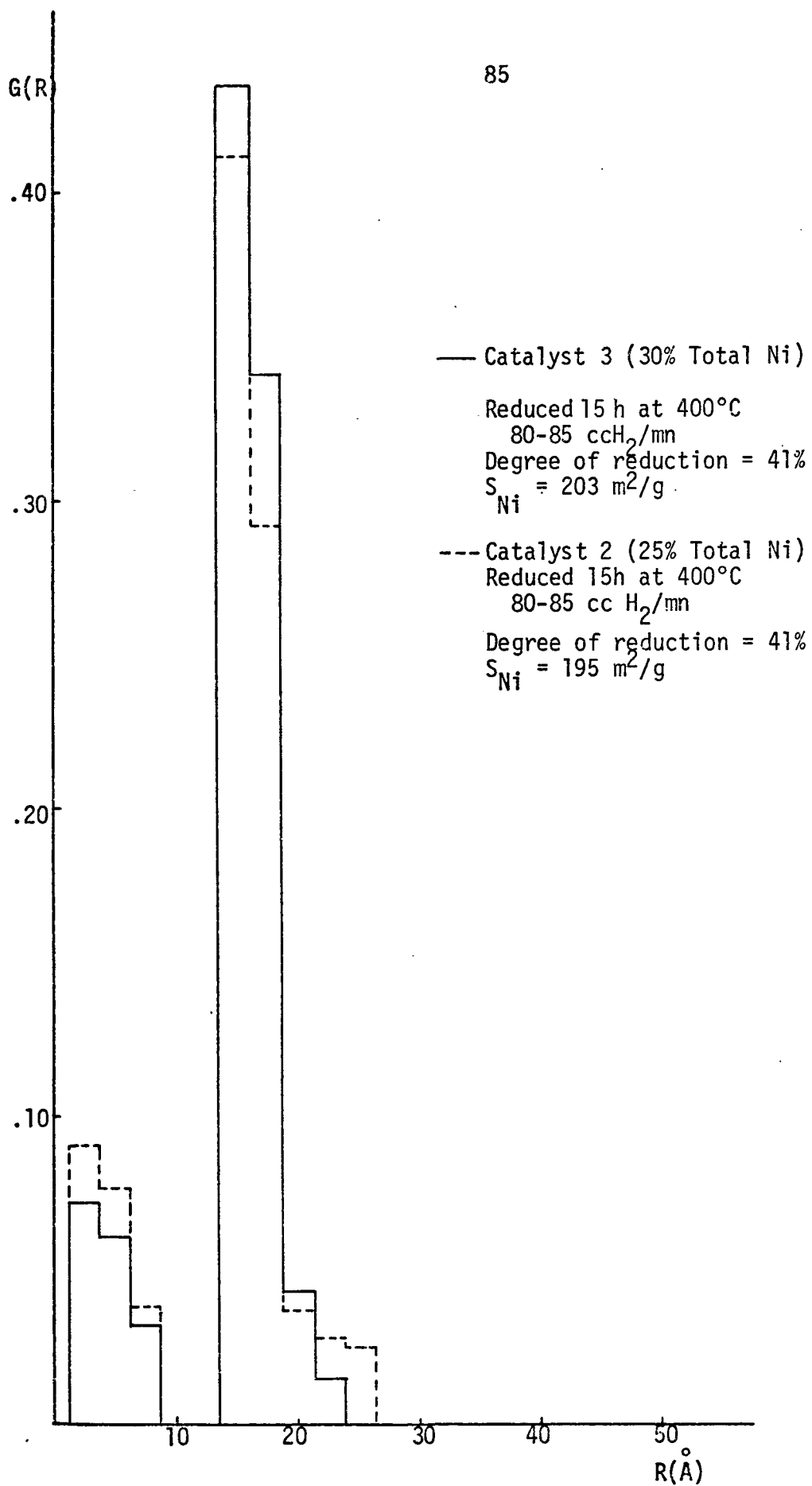


Fig. 851

Finally, a comparison with other classical preparation methods is useful to fully assess the advantages of the precipitation-deposition method used here.

A catalyst was prepared by impregnation following the method of Taylor.⁽²⁷⁾ The support (Cab-O-Sil HS5) was wetted by the required amount of water and impregnated with a solution of nickel nitrate. After drying in air at 120°C overnight, the catalyst called catalyst E had 16% nickel.

After reduction at 400°C for 15 hours in hydrogen (20-25 cc/mn) catalyst E (16% nickel) compared with catalyst 1 (17% nickel) reduced in similar conditions.

Fig. 852 shows how badly dispersed the impregnated sample E is compared to its counterpart. The range of radii had to be shifted toward larger values (from 22.5 Å to 70 Å) to show that many crystallites are more than 50 Å in radius. The peak at the lower end of the scale (22.5 Å) means that about 23% of the crystallites are less than 22.5 Å. Catalyst E has two groups of crystallites very distinct in size. As expected, catalyst E is almost completely reduced since the nickel-support interaction is very weak.

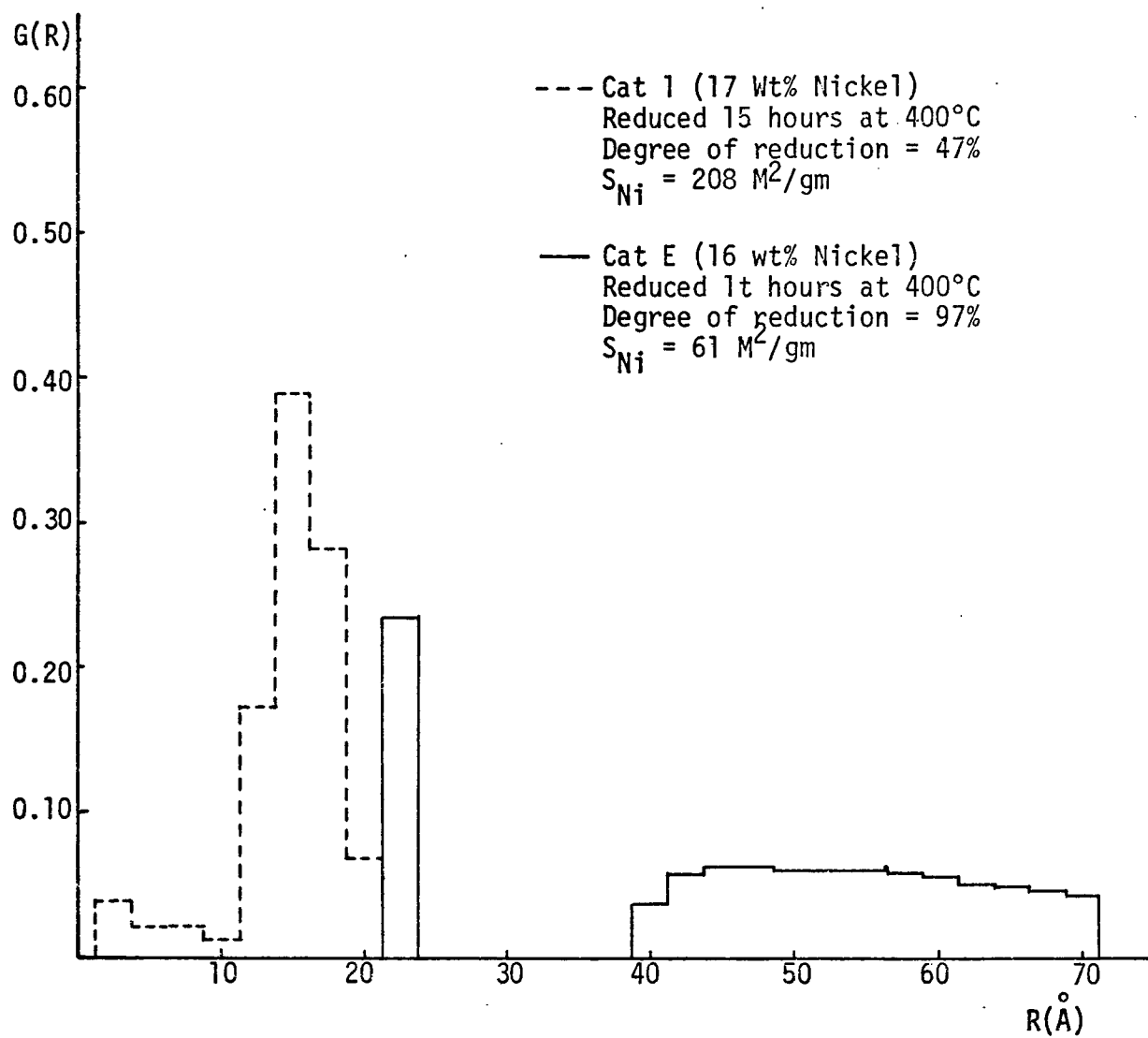


Fig. 852

86. Conclusion and Recommendations

The method of precipitation-deposition investigated in this work has proved very efficient in producing nickel on silica catalysts with a uniform dispersion of small nickel crystallites. The interaction between the precipitating nickel and the silica is the key to achieve this result. A solution of nickel nitrate (0.14M) and solid silica (7.6 gm/l Cab-O-Sil HS5) yields uniformly and highly dispersed catalysts when urea (0.42M) is added at 90°C. The slow decomposition of urea brings about a homogeneous increase in hydroxyl ions and the precipitation proceeds at low degrees of saturation. After four hours precipitation time, the nickel content of the final product reaches 25-30 wt%. When attempting to achieve higher nickel content (either by increasing the precipitation time or by using a higher nickel to silica ratio solution), the resulting catalysts present a broader range of crystallite sizes with a maximum of the distribution shifted towards larger sizes.

During reduction of the catalyst in hydrogen at 400°C, high hydrogen velocities are beneficial to the catalyst. Upon increasing hydrogen flow-rate, the portion of nickel reduced to the metallic state appears to increase significantly whereas the CSD becomes even narrower with a slight shift towards smaller particles. At 400°C, increased reduction times affect the CSD very little but are desirable in obtaining more reduced nickel available. Higher reduction temperatures are detrimental to the catalyst. At 500°C, the CSD is broader and much less uniform than it is at 400°C. Calcination at 350°C or

450°C prior to reduction did not apparently affect the dispersion of a well dispersed sample. Finally it was found that adsorbed hydrogen or oxygen lowers the magnetization of a highly dispersed catalyst to a large extent. Care must be taken to remove chemisorbed gases before magnetic measurements. When oxygen is the adsorbate (as it is during a typical passivation operation), it can be removed from the catalyst by a mild reduction without a significant change in the CSD.

Not only the precipitation-deposition method yields uniform CSD but moreover the preparation is easily controlled and as a result, reproducible. In addition, due to its homogeneous nature, the method will be particularly convenient to scale-up.

There are admittedly a few weaknesses in the CSD experimental measurements. First of all, the catalysts were assumed to be superparamagnetic in order to use the Langevin equation and computing the distribution coefficients. This assumption is reasonable in view of the results indicating particle sizes well below 200 Å in diameter (the limit for superparamagnetic behavior). Nonetheless, the undeniable proof of superparamagnetism is the superposition of the M vs. H/T curves at different temperatures.⁽²⁰⁾ Magnetic measurements in this work were possible only at room temperature, but a modified apparatus would allow to vary the temperature in a future work.

The second weakness is related to the absence of very low temperature data, the value of the saturation magnetization was indirectly determined from a sintered sample. The high temperature treatment needed to sinter the samples could have had some side effects even

in inert atmosphere (for instance, loss of nickel upon reaction with decomposition products). However, considering that two nickel catalysts sintered for different times had identical magnetization curves, these effects are unlikely.

In future work, involving expensive and time consuming experimental procedure, low temperature data measurements would be desirable to check the low-field data obtained in this work. Better accuracy and more reliable values of the saturation magnetization would pay for the additional effort.

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APPENDIX

APPENDIX A

Sintering Mechanisms

Particle Migration Model

Ruckenstein and Pulvermacher (R&P) treated the particles as migrating species which coalesce upon collision.^(9,10) They find two limiting cases: growth controlled by particle migration and growth controlled by coalescence. In both cases, their solutions for the rate of change of the exposed surface area A are expressions of the form:

$$\frac{dS}{dt} = -KS^n$$

The exponent n varies from 1 to 3 for coalescence control and from 4 to 8 for particle migration control. Particle migration control is associated with strong interactions between metal and support while in coalescence control there is a weaker metal-support interaction. Model predictions for the value of n in the rate of surface area decay are consistent with experimental data. Effect of atmosphere on particle growth is interpreted by a modification of the wetting angle of the metal crystallite lying on the support.

The evolution of particle size distribution has been predicted for several assumptions. They found that for energetically homogeneous surfaces the distribution reaches a stationary limit when sintering is controlled by particle migration. This limit distribution is

independent of initial distribution after long period of time and can be represented by a universal curve using dimensionless variables.⁽⁹⁾ No stationary limit is obtained for coalescence control case. At last they proposed procedures to identify the rate determining step from experiment,⁽¹¹⁾ and studied the effect of pore size on their model predictions.⁽¹²⁾

One of the most significant feature in the R&P model is that all particles are to grow, so that no particle smaller than the minimum initial size can be generated. However, Flynn and Wanke objected that redispersion has been observed under certain conditions during sintering and in turn they developed a model which accounts for redispersion.⁽¹⁴⁾

Interparticle Transport Model

Besides the problem mentioned above, Flynn & Wanke found several difficulties in the R&P formalism. They argue that migration is unlikely to occur for particle size of the order of 300 Å although Pt particles on Alon support with size in this range continue to grow. Lack of evidence for crystallite migration on the support and inability of the R&P model to predict redispersion led Flynn and Wanke to derive the interparticle transport model which consists of three steps: One, individual atoms or molecules escape from the metal crystallite to the surface of the support; two, the metal atoms migrate over the support surface; three, the migrating atoms are either captured by collision with a metal particle or are immobilized by encountering an energy well on the support surface. After discussion of the

reliability of these assumptions, the authors derive equations for quantitative information on the rate of change in particle sizes.

Their basic conclusions are:

1. The shape of the initial distribution will affect the overall rate of sintering. Unisized particles do not sinter at all, whereas they will sinter readily in the R&P model.

2. Redispersion can occur so that at least during the early stages of sintering the average surface area may exhibit a maximum.

3. Nature of atmosphere affects the rate of particle growth by changing the character of the escaping species and the interaction between metal atoms and the support.

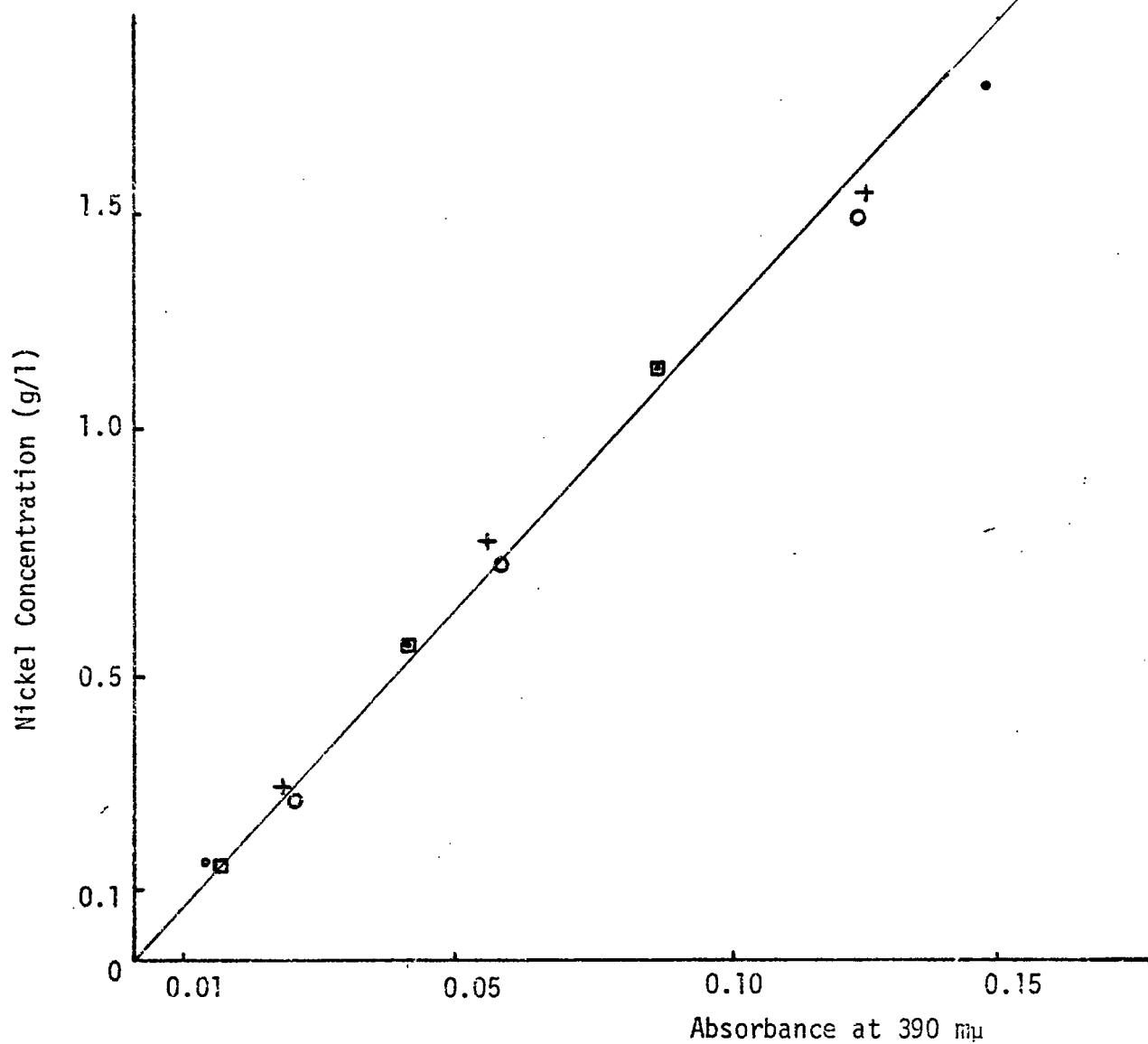
4. Order of sintering rate in the equation $\frac{dS}{dt} = -KS^n$ can be negative (when redispersion occur) and can be as high as 15. n should be higher for a wide size distribution than for a narrow one.

In a more recent work,⁽¹³⁾ Flynn and Wanke conducted an experimental study of sintering of supported platinum catalysts. Their findings were consistent with the interparticle transport model but they were not conclusive enough to rule out a possible particle migration model.

In view of these comments, it appears clearly that careful experimental work is needed to clarify the problem. The complexity arises to a large extent from the very fact that the particles are distributed in size and the measurement of this distribution is subject to large error in usual techniques. By starting with a unisized distribution of particles and following its evolution during the sintering process with accurate measurement, there is hope to discriminate between the possible mechanisms.

Appendix B

Standard Nickel Solutions for Colorimetry



• Nickel nitrate dissolved in HCl

□ Nickel nitrate dissolved in HNO_3

+ Nickel powder dissolved in HCl

○ Nickel powder dissolved in HNO_3

APPENDIX C

Model Calculations of Crystallite Size Distributions

Various size distributions were assumed and the relative magnetization values calculated over a range of fields. These values were used as data to the computer program which calculated the distribution coefficients. The distributions were chosen to be close to actual results, except for the distribution shown in Fig. C6.

At low fields, the magnetization values were taken at the following fields (in Kgauss): .25, .5, .75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5 and 8.0. Those values are the same used in all calculations of distribution throughout this work. At high fields the values of relative magnetization were the same as above multiplied by 10 (2.5 to 80 Kgauss). The distributions are shown as histograms with 20 coefficients on 20 intervals of radii. Each interval has a length of $2.5 \text{ \AA}$. Each distribution coefficient is the average relative number of particles within a given interval.

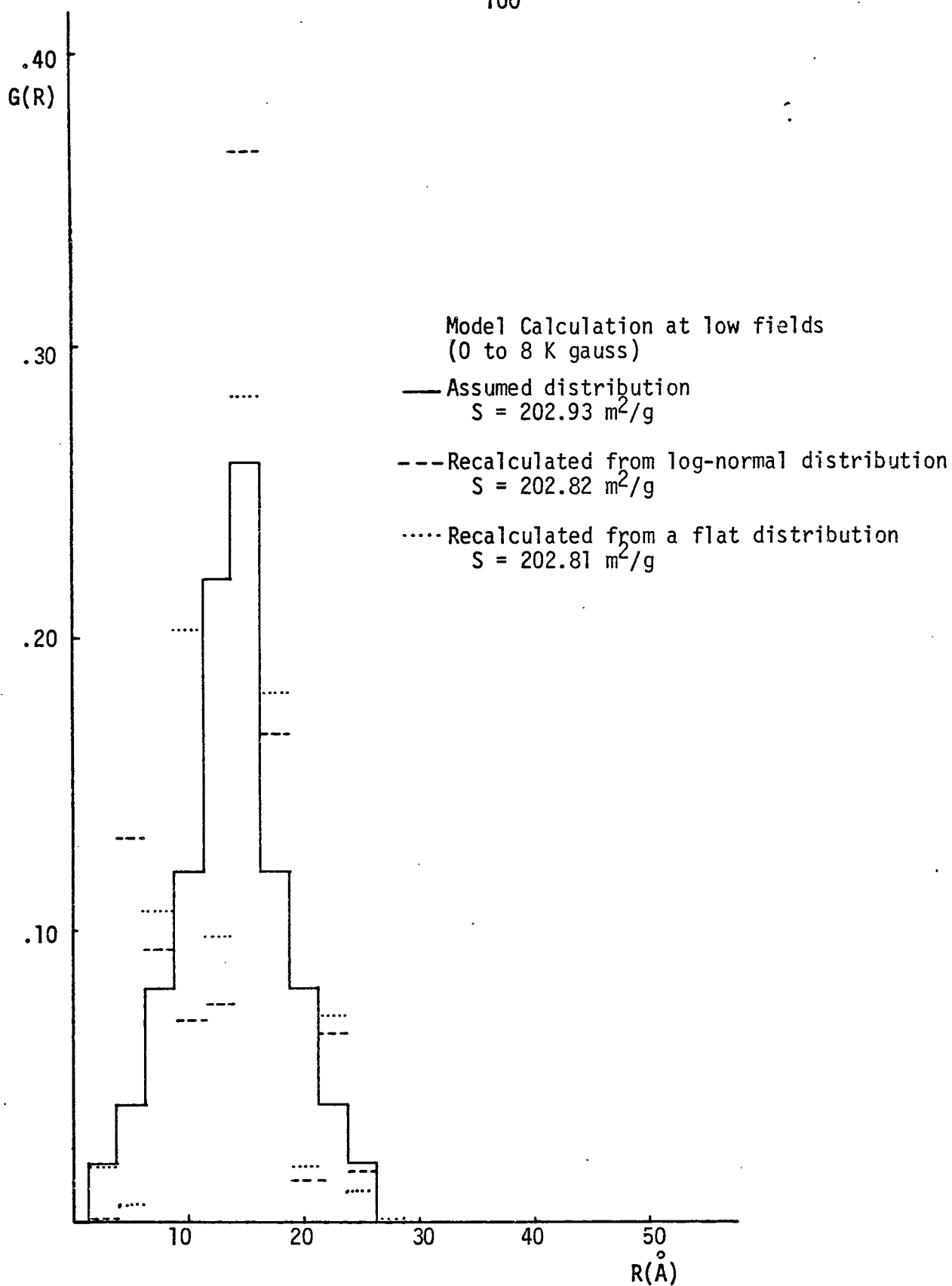
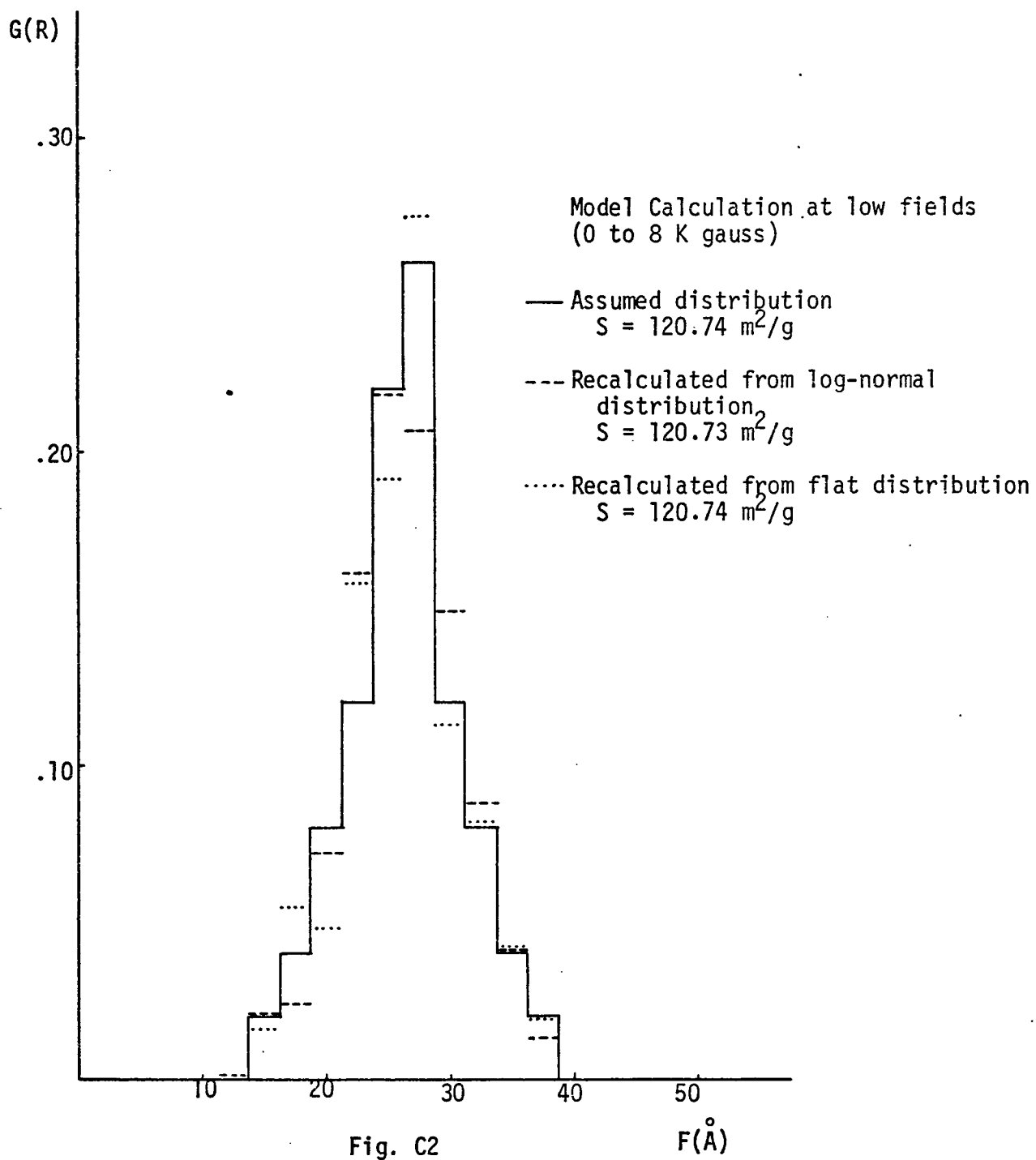


Fig. C1



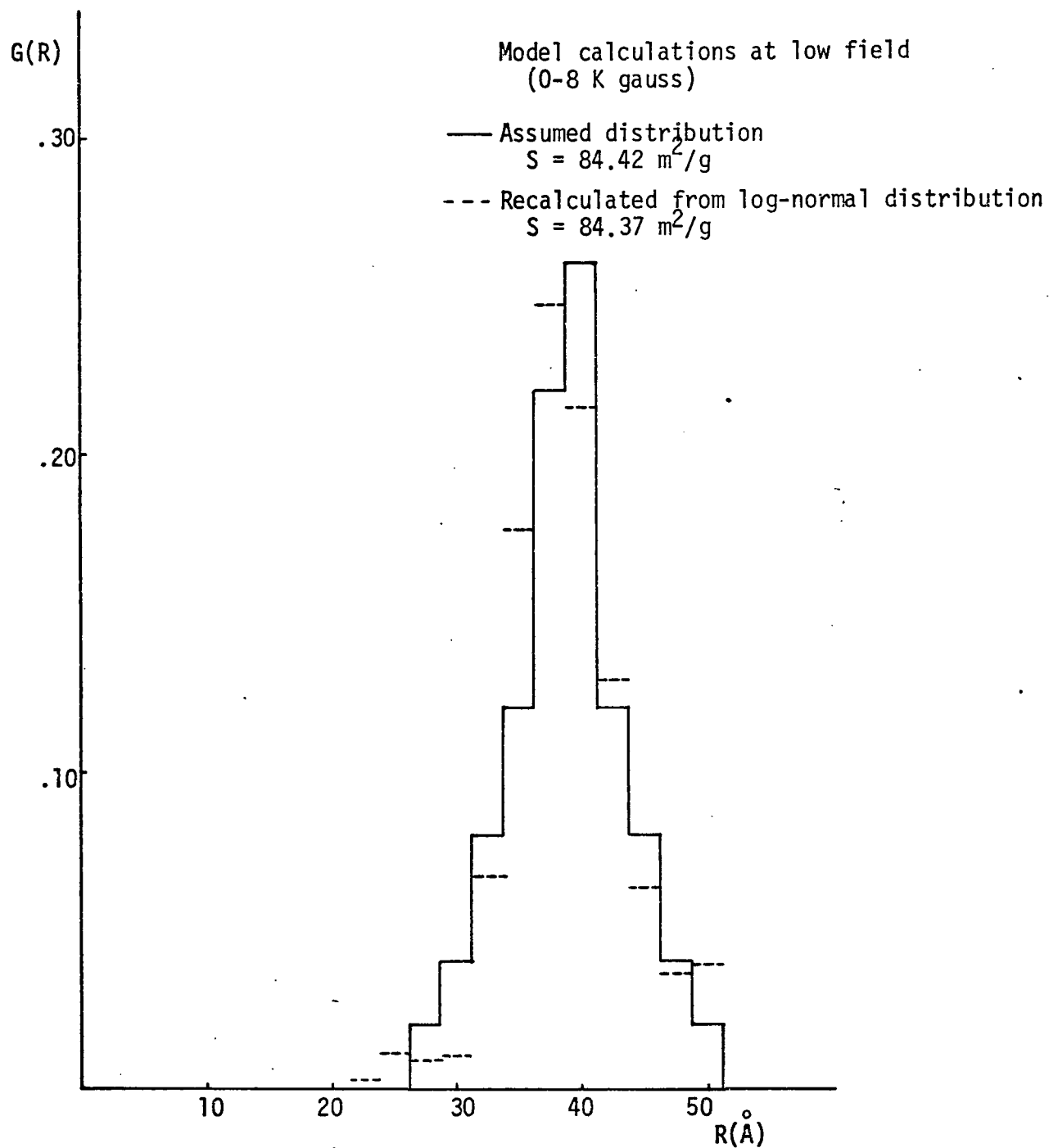


Fig. C3

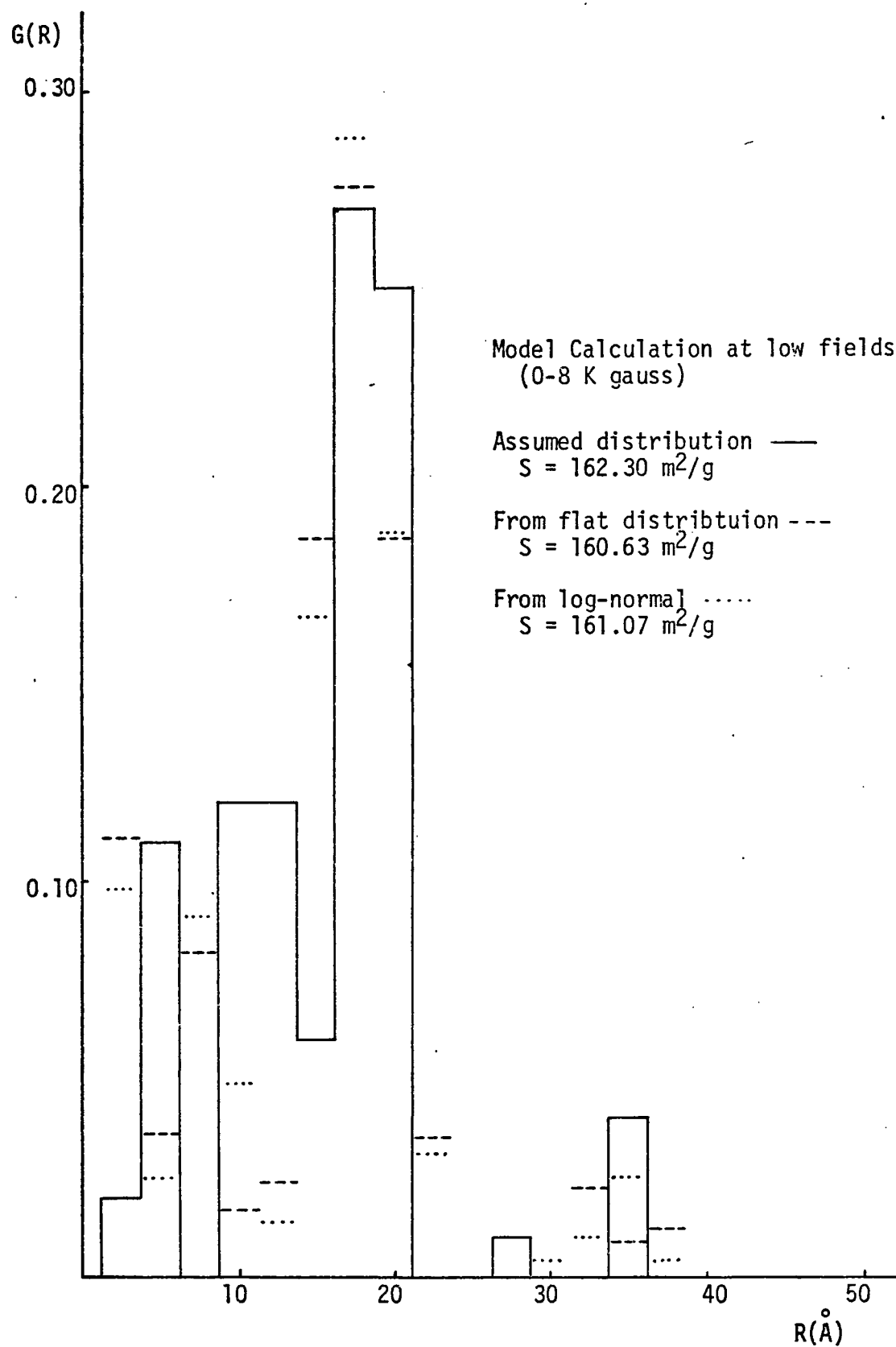


Fig. C4

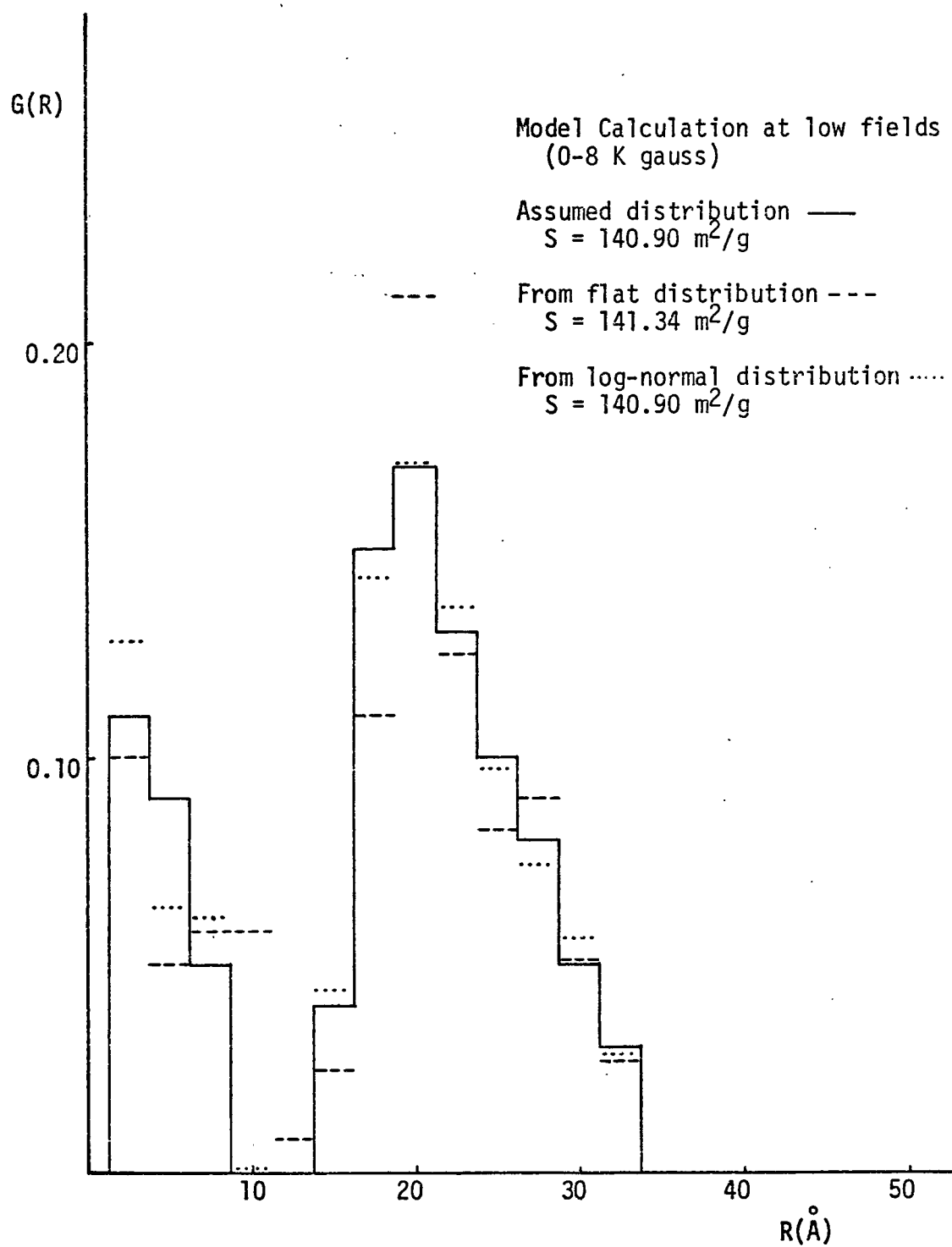


Fig. C5

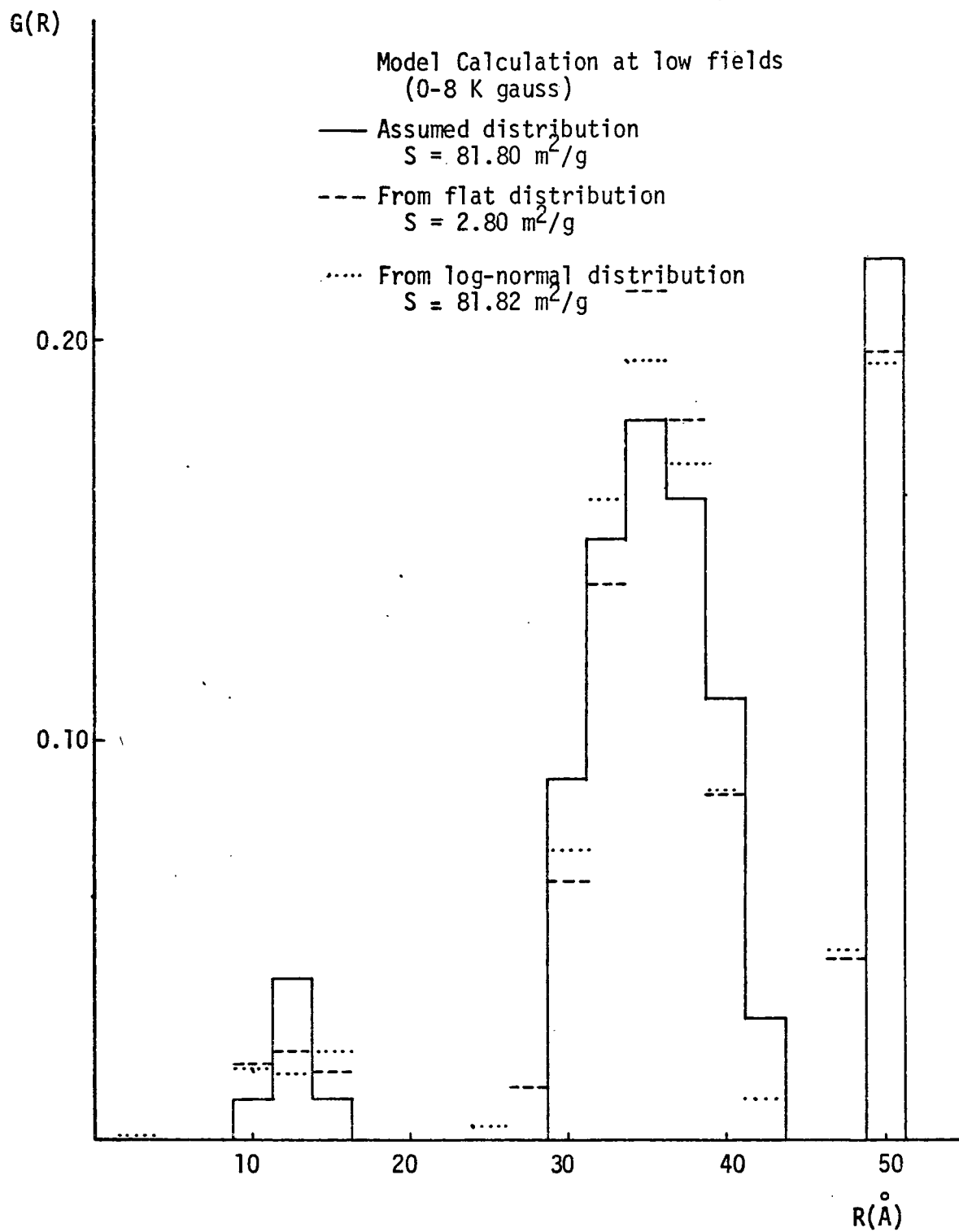


Fig. C6

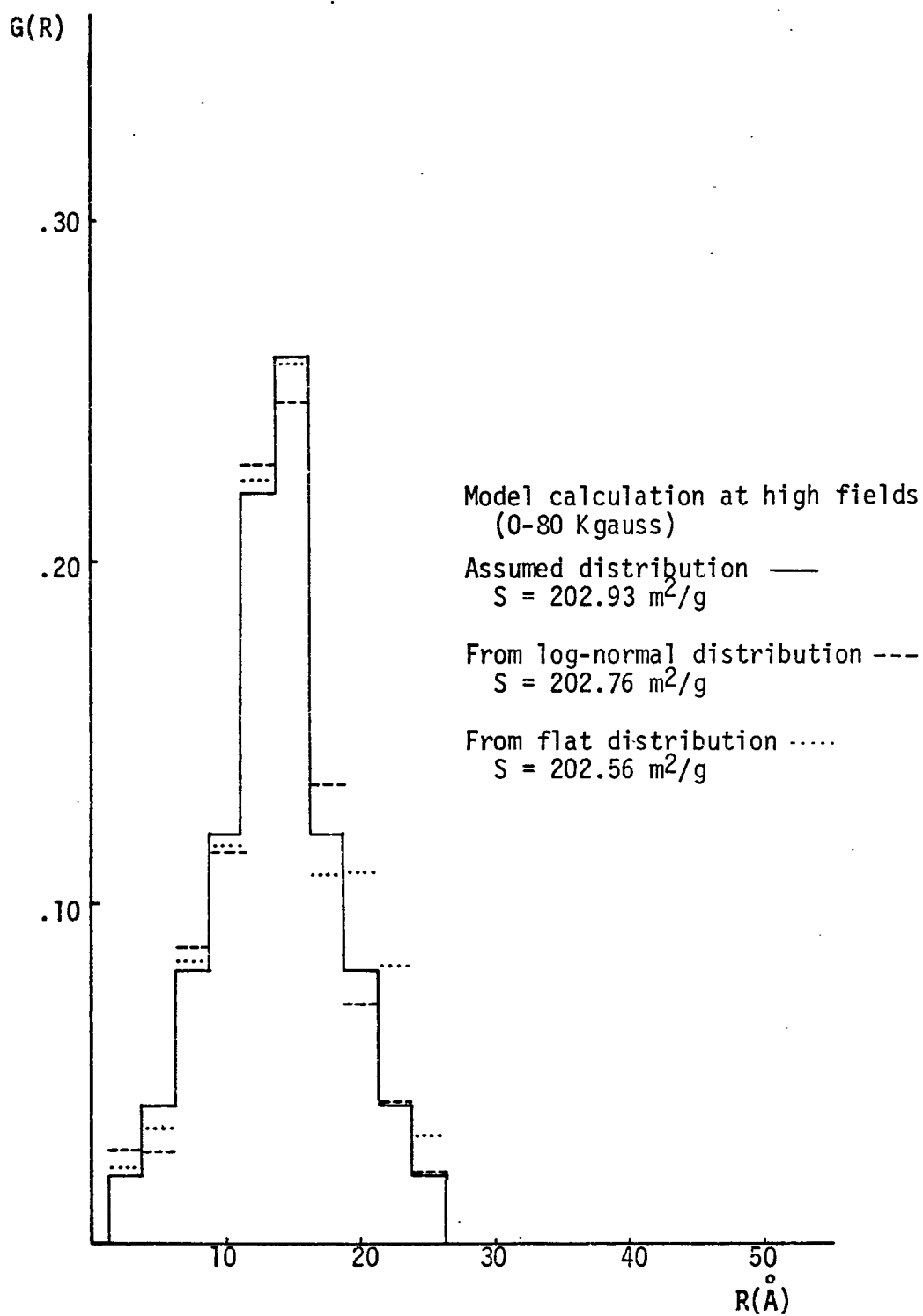


Fig. C7

APPENDIX D

Magnetization Data and CSD Coefficients

Experimental magnetization data relative to the crystallite size distributions shown in Section 8 are given in this appendix.

Each table refers to a catalyst whose characteristics can be found easily in the text. Listed data include:

H	Value of the magnetic field strength (Kilo gauss)
S	Crude experimental data for magnetization (mV) at field-strength H
M	Magnetization values used to calculation the CSD obtained by drawing the curve through experimental points (mV)
SS	Experimental magnetization of sintered sample (mV) at field H, from which M_{∞} is obtained.
M_{∞}	Value of saturation magnetization from SS vs. H curve (mV)
M/M_{∞}	Relative magnetization values at field H.
R	Crystallite Radius ($\text{\AA}$)
G(R)	Average distribution coefficient over the interval $[R-1.25, R+1.25]$

<u>H</u>	<u>S</u>	<u>M</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.05	.045	---	.0204	2.5	.12343
.5	.1	.09	2.0	.0409	5.0	.09308
.75	.1	.135	---	.0614	7.5	.03610
1.0	.15	.18	2.2	.0818	10.0	.0
1.25	.2	.22	---	.1	12.5	.0
1.5	.3	.26	2.2	.1182	15.0	.19147
1.75	.3	.30	---	.1364	17.5	.35651
2.0	.3	.335	2.2	.1523	20.0	.12952
2.5	.4	.405	2.15	.1841	22.5	.03232
3.0	.5	.47	2.2	.2136	25.0	.00807
3.5	.5	.53	2.2	.2409	27.5	.00114
4.0	.6	.59	2.2	.2682	30.0	.00650
4.5	.7	.65	2.2	.2955	32.5	.01240
5.0	.7	.70	2.2	.3182	35.0	.00944
5.5	.7	.74	2.2	.3364	37.5	.0
6.0	.8	.79	2.2	.3591	40.0	.0
6.5	.85	.83	2.2	.3773	42.5	.0
7.0	.85	.87	2.3	.3955	45.0	.0
7.5	.9	.905	2.3	.4114	47.5	.0
8.0	1.0	.94	2.3	.4273	50.0	.0

$M_{\infty} = 2.2$

TABLE D1

Catalyst 2 (418 mg)

Data and CSD for Fig. 8111 (full lines)
 Fig. 813 (dotted lines)
 Fig. 8211 (dotted lines)
 Fig. 8231 (dotted lines)
 Fig. 83 (dotted lines)

<u>H</u>	<u>S</u>	<u>M</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.05	.11	---	.0344	2.5	.15584
.5	.25	.22	2.8	.0688	5.0	.13203
.75	.35	.33	---	.1031	7.5	.03900
1.0	.5	.44	3.05	.1375	10.0	.0
1.25	.6	.54	---	.1688	12.5	.0
1.5	.6	.63	3.05	.1969	15.0	.0
1.75	.7	.71	---	.2219	17.5	.10459
2.0	.8	.80	3.1	.2469	20.0	.18434
2.5	.9	.92	3.1	.2875	22.5	.15424
3.0	1.0	1.03	3.1	.3219	25.0	.09324
3.5	1.1	1.13	3.1	.3531	27.5	.05907
4.0	1.2	1.22	3.1	.3813	30.0	.04701
4.5	1.3	1.3	3.1	.4063	32.5	.03063
5.0	1.4	1.37	3.2	.4281	35.0	.0
5.5	1.4	1.43	3.15	.4469	37.5	.0
6.0	1.5	1.48	3.2	.4625	40.0	.0
6.5	1.5	1.52	3.2	.4750	42.5	.0
7.0	1.6	1.56	3.3	.4875	45.0	.0
7.5	1.7	1.6	3.2	.5	47.5	.0
8.0	1.7	1.63	3.3	.5094	50.0	.0

$M_{\infty} = 3.2 \text{ mV}$

TABLE D2

Catalyst 4 (558 mg)

Data and CSD for Fig. 8112

Fig. 8212 (dotted lines)

Fig. 8233 (dotted lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.2	---	.054	2.5	.0
.5	.45	3.7	.107	5.0	.0
.75	.6	---	.160	7.5	.0
1.0	.85	4.0	.202	10.0	.0
1.25	1.05	---	.250	12.5	.11124
1.5	1.25	4.1	.286	15.0	.20863
1.75	1.3	---	.314	17.5	.16695
2.0	1.4	4.05	.345	20.0	.07832
2.5	1.6	4.1	.393	22.5	.03524
3.0	1.8	4.1	.433	25.0	.05221
3.5	1.9	4.1	.457	27.5	.08972
4.0	2.0	4.15	.488	30.0	.10915
4.5	2.1	4.15	.512	32.5	.0985
5.0	2.2	4.2	.536	35.0	.05313
5.5	2.4	4.2	.560	37.5	.0
6.0	2.45	4.2	.579	40.0	.0
6.5	2.55	4.2	.600	42.5	.0
7.0	2.65	4.25	.619	45.0	.0
7.5	2.7	4.3	.636	47.5	.0
8.0	2.8	4.25	.650	50.0	.0

$M_{\infty} = 4.2$

TABLE D3 Catalyst 5 (465 mg)

Reference to Figures 8113 and Fig. 8213 (Dotted Lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.25	---	.050	2.5	.04250
.5	.5	3.9	.100	5.0	.04056
.75	.7	---	.161	7.5	.04064
1.0	.85	4.25	.194	10.0	.04272
1.25	1.0	---	.233	12.5	.06450
1.5	1.2	4.35	.267	15.0	.09287
1.75	1.3	---	.300	17.5	.10202
2.0	1.4	4.35	.322	20.0	.09410
2.5	1.7	4.4	.367	22.5	.08939
3.0	1.8	4.35	.411	25.0	.09145
3.5	2.0	4.4	.444	27.5	.09116
4.0	2.1	4.4	.467	30.0	.08417
4.5	2.2	4.4	.489	32.5	.06988
5.0	2.3	4.45	.511	35.0	.04574
5.5	2.4	4.5	.533	37.5	.00827
6.0	2.45	4.5	.544	40.0	.0
6.5	2.5	4.5	.567	42.5	.0
7.0	2.6	4.5	.578	45.0	.0
7.5	2.7	4.55	.589	47.5	.0
8.0	2.8	4.6	.600	50.0	.0

$M_{\infty} = 4.5$

TABLE D 4 Catalyst 6 (556 mg)

Refers to Fig. 8114 and Fig. 8214 (Dotted Lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.15	---	.044	2.5	.0
.5	.45	4.3	.088	5.0	.00004
.75	.7	---	.127	7.5	.00004
1.0	.95	4.8	.167	10.0	.00566
1.25	1.1	---	.206	12.5	.07023
1.5	1.3	4.9	.245	15.0	.12754
1.75	1.4	---	.275	17.5	.17178
2.0	1.55	5.0	.294	20.0	.18138
2.5	1.8	5.0	.363	22.5	.15502
3.0	2.1	5.0	.402	25.0	.11960
3.5	2.3	5.05	.446	27.5	.08724
4.0	2.4	5.0	.480	30.0	.05609
4.5	2.6	5.0	.510	32.5	.02536
5.0	2.75	5.0	.539	35.0	.0
5.5	2.9	5.0	.569	37.5	.0
6.0	3.05	5.0	.588	40.0	.0
6.5	3.1	5.1	.608	42.5	.0
7.0	3.2	5.1	.627	45.0	.0
7.5	3.4	5.1	.647	47.5	.0
8.0	3.4	5.2	.667	50.0	.0

$M_{\infty} = 5.2$

TABLE D5 Catalyst 7 (531 mg)
Fig. 8115 and 8141 (Dotted Lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.1	---	.0323	2.5	.10834
.5	.2	2.7	.0710	5.0	.09366
.75	.35	---	.1032	7.5	.05518
1.0	.4	2.9	.1419	10.0	.00126
1.25	.55	---	.1710	12.5	.00210
1.5	.6	2.9	.2	15.0	.04398
1.75	.7	---	.2258	17.5	.15345
2.0	.8	3.0	.2548	20.0	.16949
2.5	.9	3.0	.2968	22.5	.12857
3.0	1.0	3.0	.3355	25.0	.09606
3.5	1.1	3.0	.3645	27.5	.07898
4.0	1.2	3.0	.3935	30.0	.05544
4.5	1.3	3.0	.4194	32.5	.01354
5.0	1.4	3.0	.4452	35.0	.0
5.5	1.5	3.05	.4645	37.5	.0
6.0	1.5	3.05	.4839	40.0	.0
6.5	1.5	3.1	.4968	42.5	.0
7.0	1.6	3.1	.5129	45.0	.0
7.5	1.6	3.1	.5258	47.5	.0
8.0	1.7	3.1	.5387	50.0	.0

$M_{\infty} = 3.1$

TABLE D6 Catalyst 8 (227 mg)

Fig. 8116
8142 (dotted lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.1	---	.046	2.5	.09085
.5	.4	3.3	.090	5.0	.06608
.75	.5	---	.133	7.5	.03411
1.0	.65	3.7	.172	10.0	.0
1.25	.8	---	.205	12.5	.0
1.5	.9	3.7	.241	15.0	.05138
1.75	1.1	---	.269	17.5	.15229
2.0	1.2	3.7	.295	20.0	.18589
2.5	1.35	3.75	.338	22.5	.14412
3.0	1.45	3.75	.379	25.0	.08483
3.5	1.6	3.75	.415	27.5	.05286
4.0	1.75	3.8	.446	30.0	.04680
4.5	1.85	3.8	.472	32.5	.04560
5.0	1.95	3.8	.495	35.0	.03384
5.5	2.0	3.85	.518	37.5	.01134
6.0	2.1	3.8	.536	40.0	.0
6.5	2.15	3.8	.551	42.5	.0
7.0	2.2	3.8	.569	45.0	.0
7.5	2.3	3.8	.579	47.5	.0
8.0	2.35	3.85	.590	50.0	.0

$M_{\infty} = 3.9$

TABLE D7 Catalyst 9 (226 mg)

Figure 8117
8234 (dotted lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.0	---	.014	2.5	.03592
.5	.05	1.5	.029	5.0	.02031
.75	.05	---	.043	7.5	.02072
1.0	.1	1.6	.057	10.0	.01353
1.25	.15	---	.074	12.5	.17909
1.5	.15	1.7	.086	15.0	.38811
1.75	.2	---	.103	17.5	.28275
2.0	.25	1.7	.120	20.0	.06698
2.5	.25	1.65	.149	22.5	.0
3.0	.3	1.65	.177	25.0	.0
3.5	.35	1.65	.206	27.5	.0
4.0	.4	1.7	.234	30.0	.0
4.5	.4	1.7	.257	32.5	.0
5.0	.5	1.7	.280	35.0	.0
5.5	.55	1.7	.303	37.5	.0
6.0	.6	1.7	.326	40.0	.0
6.5	.6	1.7	.349	42.5	.0
7.0	.6	1.7	.366	45.0	.0
7.5	.65	1.7	.383	47.5	.0
8.0	.7	1.75	.4	50.0	.0

$M_{\infty} = 1.75 \text{ mV}$

TABLE D8 Catalyst 1 (347 mg)
Fig. 813

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.0	---	.217	2.5	.0
.5	3.5	5.0	.370	5.0	.0
.75	4.5	---	.489	7.5	.00009
1.0	5.4	6.9	.576	10.0	.00815
1.25	5.9	6.9	.641	12.5	.04547
1.5	6.4	8.1	.690	15.0	.00725
1.75	6.7	---	.723	17.5	.0
2.0	6.85	8.6	.750	20.0	.0
2.5	7.3	8.8	.788	22.5	.0
3.0	7.45	8.9	.815	25.0	.0
3.5	7.64	9.0	.826	27.5	.0
4.0	7.8	9.0	.842	30.0	.08924
4.5	7.9	9.0	.859	32.5	.15514
5.0	8.0	9.0	.870	35.0	.17439
5.5	8.1	9.0	.880	37.5	.15962
6.0	8.2	9.05	.886	40.0	.12776
6.5	8.4	9.1	.891	42.5	.09262
7.0	8.4	9.1	.897	45.0	.06311
7.5	8.4	9.2	.902	47.5	.04333
8.0	8.6	9.3	.908	50.0	.03386

$M_{\infty} = 9.2$

TABLE D9 Catalyst 10 (800 mg)

Fig. 8141

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	4.5	---	.3241	2.5	.02018
.5	6.3	6.4	.4276	5.0	.0
.75	8.2	---	.5586	7.5	.0
1.0	9.3	10.0	.6414	10.0	.0
1.25	10.3	---	.7103	12.5	.0
1.5	10.9	12.1	.7517	15.0	.0
1.75	11.4	---	.7862	17.5	.0
2.0	11.8	13.3	.8138	20.0	.0
2.5	12.3	13.8	.8483	22.5	.0
3.0	12.6	14.2	.8690	25.0	.0
3.5	12.8	14.4	.8828	27.5	.0
4.0	12.9	14.45	.8897	30.0	.07236
4.5	13.0	14.5	.8966	32.5	.18003
5.0	13.2	14.5	.9034	35.0	.16217
5.5	13.2	14.5	.9103	37.5	.09129
6.0	13.4	14.5	.9172	40.0	.02476
6.5	13.4	14.5	.9207	42.5	.0
7.0	13.5	14.5	.9241	45.0	.03469
7.5	13.6	14.5	.9276	47.5	.13170
8.0	13.6	14.55	.9310	50.0	.28293

$M_{\infty} = 14.5 \text{ mV}$

TABLE D10 Catalyst 11 (748 mg)

Fig. 8142

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.0	---	.040	2.5	.01844
.5	.15	1.6	.075	5.0	.04534
.75	.2	---	.110	7.5	.06272
1.0	.3	1.9	.140	10.0	.09303
1.25	.3	---	.165	12.5	.15204
1.5	.35	1.9	.190	15.0	.15482
1.75	.4	---	.215	17.5	.08848
2.0	.5	1.25	.240	20.0	.03409
2.5	.8	1.9	.280	22.5	.05003
3.0	.6	2.0	.310	25.0	.10098
3.5	.7	2.0	.335	27.5	.11531
4.0	.7	2.0	.360	30.0	.07051
4.5	.7	2.0	.385	32.5	.0
5.0	.8	2.0	.400	35.0	.0
5.5	.8	2.0	.420	37.5	.0
6.0	.9	2.0	.440	40.0	.0
6.5	.8	2.0	.450	42.5	.0
7.0	.9	2.0	.465	45.0	.0
7.5	1.0	2.05	.480	47.5	.0
8.0	1.0	2.05	.490	50.0	.01408

$M_{\infty} = 2.0 \text{ mV}$

TABLE D11 Catalyst 2 (219 mg)

Fig. 8211 (full lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.25	---	.0769	2.5	.07496
.5	.5	2.6	.1477	5.0	.06158
.75	.7	---	.2092	7.5	.02645
1.0	.8	3.0	.2585	10.0	.0
1.25	1.0	---	.2985	12.5	.0
1.5	1.1	3.1	.3323	15.0	.0
1.75	1.15	---	.3631	17.5	.10589
2.0	1.3	3.1	.3908	20.0	.17128
2.5	1.4	3.1	.4369	22.5	.15528
3.0	1.5	3.1	.4738	25.0	.09381
3.5	1.6	3.15	.5108	27.5	.04283
4.0	1.7	3.2	.5385	30.0	.02689
4.5	1.9	3.2	.5662	32.5	.03740
5.0	1.95	3.2	.5846	35.0	.05458
5.5	2.0	3.2	.6031	37.5	.06305
6.0	2.05	3.25	.6215	40.0	.05518
6.5	2.1	3.25	.6338	42.5	.03066
7.0	2.1	3.25	.6462	45.0	.0
7.5	2.15	3.25	.6585	47.5	.0
8.0	2.15	3.3	.6708	50.5	.0

$M_{\infty} = 3.25 \text{ mV}$

TABLE D12 Catalyst 4 (270 mg)

Fig. 8212 (Full lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.6	---	.1132	2.5	.0
.5	1.2	4.3	.2264	5.0	.0
.75	1.45	---	.2736	7.5	.0
1.0	1.7	4.8	.3302	10.0	.0
1.25	1.9	---	.3774	12.5	.00912
1.5	2.2	5.0	.4151	15.0	.14891
1.75	2.3	---	.4434	17.5	.15936
2.0	2.4	5.1	.4623	20.0	.11301
2.5	2.6	5.1	.5094	22.5	.07528
3.0	2.9	5.2	.5472	25.0	.05650
3.5	3.1	5.2	.5849	27.5	.04827
4.0	3.2	5.15	.6132	30.0	.04569
4.5	3.3	5.2	.6321	32.5	.04519
5.0	3.4	5.2	.6509	35.0	.04473
5.5	3.6	5.1	.6698	37.5	.04428
6.0	3.7	5.3	.6887	40.0	.04477
6.5	3.7	5.25	.7075	42.5	.04618
7.0	3.8	5.3	.7264	45.0	.04606
7.5	3.9	5.3	.7358	47.5	.04168
8.0	4.0	5.3	.7453	50.0	.03109

$M_{\infty} = 5.3 \text{ mV}$

TABLE D13 Catalyst 5 (320 mg)

Fig. 8213 (full lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.65	---	.1262	2.5	.03217
.5	1.2	4.3	.2330	5.0	.04926
.75	1.6	---	.3107	7.5	.0
1.0	1.9	4.8	.3689	10.0	.0
1.25	2.2	---	.4078	12.5	.0
1.5	2.3	5.0	.4466	15.0	.0
1.75	2.45	---	.4757	17.5	.10022
2.0	2.6	5.1	.5049	20.0	.17669
2.5	2.8	5.0	.5437	22.5	.13933
3.0	3.05	5.1	.5825	25.0	.05971
3.5	3.2	5.1	.6117	27.5	.00676
4.0	3.3	5.1	.6408	30.0	.0
4.5	3.4	5.1	.6602	32.5	.02471
5.0	3.5	5.1	.6796	35.0	.06073
5.5	3.6	5.1	.699	37.5	.09009
6.0	3.7	5.1	.7184	40.0	.10208
6.5	3.7	5.1	.7282	42.5	.09114
7.0	3.9	5.2	.7379	45.0	.05935
7.5	3.9	5.2	.7476	47.5	.00776
8.0	4.0	5.2	.7573	50.0	.0

$M_{\infty} = 5.15$

TABLE D14 Catalyst 6 (384 mg)
Fig. 8214 (Full lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.05	---	.0158	2.5	.09738
.5	.05	1.7	.0316	5.0	.08176
.75	.1	---	.0474	7.5	.03838
1.0	.1	1.8	.0605	10.0	.0
1.25	.1	---	.0737	12.5	.0
1.5	.2	1.8	.0895	15.0	.43135
1.75	.2	---	.1053	17.5	.28521
2.0	.3	1.8	.1184	20.0	.02497
2.5	.3	1.8	.1474	22.5	.03044
3.0	.35	1.9	.1737	25.0	.01052
3.5	.4	1.85	.2000	27.5	.0
4.0	.4	1.9	.2263	30.0	.0
4.5	.5	1.9	.2500	32.5	.0
5.0	.5	1.9	.2737	35.0	.0
5.5	.5	1.9	.2921	37.5	.0
6.0	.6	1.9	.3105	40.0	.0
6.5	.6	1.9	.3316	42.5	.0
7.0	.65	1.9	.3500	45.0	.0
7.5	.7	1.9	.3684	47.5	.0
8.0	.8	1.95	.3842	50.0	.0

$M_{\infty} = 1.9$

TABLE D15 Catalyst 2 (402 mg)

Fig. 8221

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.05	---	.0159	2.5	.10000
.5	.05	1.8	.0318	5.0	.08236
.75	.1	---	.0455	7.5	.03471
1.0	.15	2.0	.0614	10.0	.0
1.25	.2	---	.0773	12.5	.0
1.5	.2	2.1	.0909	15.0	.43791
1.75	.3	---	.1068	17.5	.27625
2.0	.3	2.0	.1227	20.0	.01931
2.5	.3	2.05	.1500	22.5	.02617
3.0	.4	2.1	.1773	25.0	.02329
3.5	.4	2.1	.2000	27.5	.0
4.0	.5	2.1	.2273	30.0	.0
4.5	.5	2.2	.2500	32.5	.0
5.0	.6	2.2	.2727	35.0	.0
5.5	.6	2.2	.2955	37.5	.0
6.0	.7	2.2	.3159	40.0	.0
6.5	.8	2.2	.3341	42.5	.0
7.0	.8	2.2	.3500	45.0	.0
7.5	.85	2.25	.3682	47.5	.0
8.0	.9	2.25	.3818	50.0	.0

$M_{\infty} = 2.2 \text{ mV}$

TABLE D16 Catalyst 2 (400 mg)

Fig. 8222

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.05	---	.0157	2.5	.09093
.5	.1	2.1	.0314	5.0	.07712
.75	.1	---	.0471	7.5	.03815
1.0	.2	2.35	.0627	10.0	.0
1.25	.2	---	.0784	12.5	.0
1.5	.3	2.4	.0961	15.0	.41170
1.75	.3	---	.1118	17.5	.29180
2.0	.3	2.4	.1275	20.0	.03711
2.5	.4	2.4	.1569	22.5	.02820
3.0	.5	2.5	.1843	25.0	.02495
3.5	.5	2.4	.2118	27.5	.0
4.0	.6	2.5	.2392	30.0	.0
4.5	.7	2.5	.2627	32.5	.0
5.0	.7	2.45	.2863	35.0	.0
5.5	.8	2.5	.3059	37.5	.0
6.0	.8	2.5	.3255	40.0	.0
6.5	.9	2.5	.3451	42.5	.0
7.0	.95	2.5	.3647	45.0	.0
7.5	1.0	2.55	.3804	47.5	.0
8.0	1.0	2.55	.3922	50.0	.0

$M_{\infty} = 2.55$

TABLE D17 Catalyst 2 (400 mg)

Fig. 8223

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.05	---	.0155	2.5	.06487
.5	.1	2.6	.0310	5.0	.05596
.75	.1	---	.0448	7.5	.04184
1.0	.2	2.8	.0621	10.0	.01647
1.25	.2	---	.0759	12.5	.06327
1.5	.3	2.8	.0931	15.0	.42263
1.75	.35	---	.1069	17.5	.25491
2.0	.4	2.8	.1207	20.0	.02567
2.5	.45	2.9	.1517	22.5	.04596
3.0	.5	2.85	.1793	25.0	.00838
3.5	.6	2.9	.2069	27.5	.0
4.0	.7	2.8	.2310	30.0	.0
4.5	.7	2.9	.2552	32.5	.0
5.0	.8	2.9	.2759	35.0	.0
5.5	.85	2.85	.2983	37.5	.0
6.0	.9	2.9	.3712	40.0	.0
6.5	1.0	2.9	.3379	42.5	.0
7.0	1.0	2.95	.3586	45.0	.0
7.5	1.1	2.9	.3759	47.5	.0
8.0	1.15	2.9	.3931	50.0	.0

$M_{\infty} = 2.9 \text{ mV}$

TABLE D18 Catalyst 2

Fig. 8231 (full lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.05	---	.0139	2.5	.09639
.5	.1	.29	.0292	5.0	.08313
.75	.15	---	.0444	7.5	.04717
1.0	.2	3.3	.0583	10.0	.00183
1.25	.3	---	.0722	12.5	.11118
1.5	.3	3.4	.0861	15.0	.33454
1.75	.4	---	.1028	17.5	.20257
2.0	.5	3.4	.1167	20.0	.06971
2.5	.5	3.5	.1444	27.5	.05357
3.0	.6	3.5	.1694	25.0	.0
3.5	.7	3.5	.1944	27.5	.0
4.0	.8	3.5	.2194	30.0	.0
4.5	.9	3.6	.2417	32.5	.0
5.0	.9	3.6	.2611	35.0	.0
5.5	1.0	3.5	.2806	37.5	.0
6.0	1.1	3.5	.3000	40.0	.0
6.5	1.2	3.6	.3194	42.5	.0
7.0	1.2	3.6	.3361	45.0	.0
7.5	1.3	3.6	.3528	47.5	.0
8.0	1.35	3.6	.3694	50.0	.0

$M_{\infty} = 3.6 \text{ mV}$

TABLE D19

Catalyst 2 (398 mg)

Fig. 8232

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.1	---	.0240	2.5	.06523
.5	.35	5.8	.0478	5.0	.05755
.75	.55	---	.0735	7.5	.03687
1.0	.7	6.4	.0993	10.0	.00128
1.25	.8	---	.1213	12.5	.00207
1.5	1.0	6.5	.1471	15.0	.14959
1.75	1.2	---	.1691	17.5	.37293
2.0	1.2	6.7	.1912	20.0	.19004
2.5	1.6	6.7	.2279	22.5	.03937
3.0	1.7	6.6	.2647	25.0	.03106
3.5	2.0	6.6	.2978	27.5	.03835
4.0	2.2	6.7	.3279	31.0	.01564
4.5	2.45	6.7	.3603	32.5	.0
5.0	2.6	6.7	.3824	35.0	.0
5.5	2.8	6.7	.4081	37.5	.0
6.0	2.95	6.7	.4301	40.0	.0
6.5	3.1	6.75	.4522	42.5	.0
7.0	3.2	6.75	.4743	45.0	.0
7.5	3.3	6.8	.4890	47.5	.0
8.0	3.5	6.8	.5074	50.0	.0

$M_{\infty} = 6.8 \text{ mV}$

TABLE D20

Catalyst 4 (560 mg)

Fig. 8233 (full lines)

Fig. 841 (curves 2 and 4)

Fig. 842 (full lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.2	---	.0429	2.5	.01965
.5	.4	4.0	.0867	5.0	.01838
.75	.6	---	.1276	7.5	.01218
1.0	.8	4.5	.1633	10.0	.00861
1.25	.95	---	.1990	12.5	.02929
1.5	1.1	4.7	.2245	15.0	.11189
1.75	1.2	---	.2551	17.5	.20891
2.0	1.3	4.7	.2806	20.0	.23110
2.5	1.6	4.7	.3265	22.5	.17133
3.0	1.8	4.7	.3724	25.0	.08781
3.5	2.0	4.7	.4133	27.5	.02897
4.0	2.2	4.7	.4490	30.0	.00574
4.5	2.35	4.7	.4796	32.5	.00581
5.0	2.5	4.7	.5102	35.0	.01356
5.5	2.6	4.8	.5347	37.5	.01892
6.0	2.7	4.8	.5561	40.0	.01788
6.5	2.8	4.8	.5765	42.5	.00995
7.0	2.9	4.9	.5969	45.0	.0
7.5	3.0	4.9	.6122	47.5	.0
8.0	3.1	4.85	.6327	50.0	.0

$M_{\infty} = 4.9$

TABLE D21

Catalyst 9 (226 mg)

Fig. 8234 (full lines)

Fig. 843 (curve 1)

Fig. 844 (full lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.0	---	.0206	2.5	.08904
.5	.0	1.4	.0412	5.0	.07145
.75	.1	---	.0647	7.5	.02164
1.0	.2	1.6	.0826	10.0	.0
1.25	.2	---	.1059	12.5	.0
1.5	.2	1.6	.1235	15.0	.14715
1.75	.25	---	.1441	17.5	.51909
2.0	.3	1.6	.1647	20.0	.08590
2.5	.3	1.6	.1941	22.5	.1894
3.0	.4	1.6	.2294	25.0	.01497
3.5	.4	1.7	.2588	27.5	.01286
4.0	.5	1.7	.2882	30.0	.01221
4.5	.6	1.7	.3176	32.5	.00671
5.0	.6	1.65	.3441	35.0	.0
5.5	.6	1.7	.3676	37.5	.0
6.0	.7	1.7	.3882	40.0	.0
6.5	.7	1.7	.4118	42.5	.0
7.0	.7	1.7	.4294	45.0	.0
7.5	.8	1.7	.4471	47.5	.0
8.0	.8	1.7	.4647	50.0	.0

$M_{\infty} = 1.7$

TABLE D22

Catalyst 2 (398 mg)

Fig. 83 (full lines)

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	.05	---	.0161	2.5	.07181
.5	.1	2.6	.0306	5.0	.06098
.75	.1	---	.0452	7.5	.03253
1.0	.2	2.8	.0613	10.0	.00003
1.25	.25	---	.0774	12.5	.00021
1.5	.3	2.8	.0919	15.0	.43527
1.75	.3	---	.1065	17.5	.34081
2.0	.4	2.9	.1226	20.0	.04364
2.5	.5	2.9	.1518	22.5	.01470
3.0	.6	2.9	.1806	25.0	.0
3.5	.7	2.95	.2097	27.5	.0
4.0	.7	3.0	.2387	30.0	.0
4.5	.85	3.0	.2645	32.5	.0
5.0	.9	2.95	.2871	35.0	.0
5.5	1.0	3.0	.3097	37.5	.0
6.0	1.0	3.0	.3323	40.0	.0
6.5	1.1	3.1	.3516	42.5	.0
7.0	1.14	3.1	.3710	45.0	.0
7.5	1.2	3.0	.3871	47.5	.0
8.0	1.3	3.1	.4032	50.0	.0

$M_{\infty} = 3.1 \text{ mV}$

TABLE D23

Catalyst 3 (400 mg)

Fig. 851

<u>H</u>	<u>S</u>	<u>SS</u>	<u>M/M_∞</u>	<u>R</u>	<u>G(R)</u>
.25	2.0	---	.3846	22.5	.23636
.5	2.8	4.2	.5288	25.0	.0
.75	3.1	---	.6058	27.5	.0
1.0	3.5	4.8	.6635	30.0	.0
1.25	3.6	---	.6923	32.5	.0
1.5	3.75	4.9	.7212	35.0	.0
1.75	3.85	---	.7404	37.5	.0
2.0	3.95	5.0	.7596	40.0	.03764
2.5	4.05	5.0	.7788	42.5	.05786
3.0	4.1	5.05	.7981	45.0	.06603
3.5	4.2	5.05	.8077	47.5	.06733
4.0	4.2	5.1	.8173	50.0	.06577
4.5	4.3	5.1	.8269	52.5	.06298
5.0	4.3	5.1	.9365	55.0	.06033
5.5	4.4	5.1	.9462	57.5	.05720
6.0	4.4	5.15	.8558	60.0	.05438
6.5	4.5	5.15	.8615	62.5	.05122
7.0	4.5	5.2	.8692	65.0	.04809
7.5	4.5	5.2	.8750	67.5	.04546
8.0	4.6	5.2	.8808	70.0	.04298

$M_{\infty} = 5.2$

TABLE D24

Catalyst E (533 mg)

Fig. 852