Item 1 of 4 Report DOE/ER/04254-4

Progress Report

"The Properties of Supported Metal Catalysts"

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Report for the Period 4/1/80 - 3/1/81

NOTICE

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Abstract:

The set of Pd/SiO_2 catalysts described in Report COO-4254-3 has been further characterized by in-situ, controlled atmosphere x-ray diffraction studies. In-situ reaction studies have also been conducted for methylcyclopropane hydrogenolysis and the formation of palladium hydride has been detected for the first time <u>during</u> a catalytic reaction.

Isotopic exchange between cyclopentane and deuterium has been investigated for the series. This reaction is structure sensitive with the turnover number increasing monotonically with percentage metal exposed. Selectivity for exchange is also structure sensitive, with the ratio of d_{10}/d_5 steadily declining with increasing percentage exposed. This change indicates rollover of cyclopentane is more difficult on smaller particles of Pd. We have also completed the study of propylene hydrogenation on our previous Pt/SiO_2 series. Some years ago we reported one set of results for this system; however, that was prior to our discovery that the structure sensitivity of the methylcycopropane and cyclopentane reactions could be altered at will by the pretreatment procedures. Similar behavior has now been found for the hydrogenation of propylene, although the patterns of structure sensitivity differ.

The mean square amplitude of vibration of the Pt atoms (measured with x-rays) has been obtained in situ in different gas environments; it has been found to <u>increase</u> with increasing temperature of H_2 reduction during pretreatment. We are now attempting to correlate this with the observed changes in sensitivity. Only for low percent Pt exposed in these catalysts, we find that Pt changes form with increasing temperature of hydrogen reduction during pretreatment. The volume fraction determined from the area of the diffraction peak decreases appreciably. An examination of the Pt fluourescent x-rays however, shows that the Pt is still present. This implies that either the Pt is dissolved in the support, or it has broken up into very fine particles. Studies

of small angle, x-ray scattering are underway; if there are fine particles these will be detected in this measurement.

WORK ACCOMPLISHED SINCE REPORT COO-4254-3 TO 1 MARCH, 1981

I. Pd/SiO$_2$ Catalysts

A. Chemical Reactivity

A complete description of the preparation and properties of the Pd/SiO$_2$ series has been given in the last report. Of this series, the bulk of our recent studies has been carried out with percentage exposures of 13.8, 29.3, 4918, 65.8 and 79.1, all prepared via ion exchange with Pd $(NH_3)_4^{2+}$.

Isotopic Exchange Between Cyclopentane and Deuterium. This reaction was investigated on all of the Pd/SiO$_2$ catalysts at a D$_2$/cyclopentane ratio of 13. Measurement on a given batch of catalyst was made at the following successive temperatures, 40, 55, 70 and 40°C. At least two samples of each catalyst were examined. A flow of D$_2$ at 40°C preceded the first determination.

When catalysts were pretreated by the standard pretreatment, O$_2$, 300°; H$_2$, 300°; He, 450°, cool in He, the overall rate of exchange was structure sensitive. At 55°C, the turnover frequency per surface atom of Pd, N_t, increased monotonically from 1.5×10^{-3} sec^{-1} on Pd/SiO$_2$ of percentage exposed, D_h, equal 29.3% to 8.78×10^{-3} sec^{-1} on 79.1%. Activation energies were all in the range 19-22 kcal mol^{-1}, that is, indistinguishable to within our experimental error.

We were unable to secure reproducible rates with 13.8% Pd/SiO$_2$ and we have not yet found the origin of the variation in activity. It does not appear to lie in varying amounts of formation of PdH since a flow of D$_2$ at 0°C before reaction did not lead to reproducible rates.

The proportions of the various exchanged species, d_1-d_{10} were also structure sensitive. In particular, although d_5 constituted a large and nearly constant fraction of all exchanged species, the ratio, d_{10}/d_5, steadily declined with increasing percentage exposed: at 55°C, from 0.4 at 29.3% to 0.2 at 79.1%. This change accords with the view that rollover is more difficult on smaller particles of Pd.

Two Pd/Al_2O_3 catalysts were also examined. One had been used for this reaction some years ago (J. Amer. Chem. Soc., 88, 4549 (1966)). It was found to have a D_h of 14.9%. N_t was a little greater than for Pd/SiO_2, but selectivities were different, in particular, d_{10}/d_5 was 1. An Engelhart Pd/Al_2O_3 (D_h = 27.8%) gave an N_t twice as large, about the same d_{10}/d_5 but the relative proportions of d_5 and d_{10} were considerably smaller.

The exchange reaction was also examined on the Pd/SiO_2 catalysts after the pretreatment O_2, 300°; D_2, 450° cool in D_2. Unlike the case of the standard pretreatment, N_t varied little with D_h and it was equal about to 2.5×10^{-3} sec^{-1}. Also, the ratio d_{10}/d_5 was nearly structure insensitive and about 0.2.

Because of problems in understanding the effect of pretreatments in which a catalyst is cooled in hydrogen from 450°C, three Pt/SiO_2 catalysts were exposed to the following pretreatment: O_2, 300°; H_2, 450°; cool in H_2 to 25°C, Ar, 25→450°, cool in Ar to 25°C. D_h was then measured by hydrogen chemisorption. Values were lower than after O_2, 300°; H_2, 300°, Ar, 450°. It appeared possible that the lowered value of D_h resulted from some form of hydrogen which adsorbs at 450°C but not at 300°C and which is not fully removed by Ar, 450°. Accordingly, samples cooled from 450°C in H_2 were heated to 450°C in flowing Ar and the amount of hydrogen which desorbed was measured. The catalyst was then heated to 500°C and the desorbed hydrogen was measured. Results are given below.

D_h	6.3%	40%	81%
H_2 at 450°	10.5	44.0	81.7
H_2 at 500°	1.6	4.8	4.7

Desorbed H_2 is given as (H atoms desorbed)/(total atoms of Pt) x 100. The catalyst of D_h = 6.3 cooled in Ar after H_2, 450° holds much more hydrogen than that corresponding to a monolayer. Some of this hydrogen is not removed in Ar at 450° during one hr. Removal at 500°C appears to be complete.

If a sample cooled in H_2 from 450°C is heated in Ar to 500°C and cooled to 25°C in Ar or if O_2, 300°; H_2, 450°→25°; Ar, 450° is treated O_2, 450°; H_2, 300°; H_2, 300°; Ar, 450° and if H_2 chemisorption is then run at 25°C, normal values of D_h are obtained for all catalysts. Thus, some form of adsorbed hydrogen is generated at 450°C which is much more strongly held than H_2 adsorbed at 25° or 300°C. In view of the effect of this hydrogen upon the apparent value of D_h, it is not likely that it is "spilled-over hydrogen" on the silica surface. Relative to Pt_s, the amount of extra adsorbed hydrogen at 450°C is the largest on the larger particles.

The apparatus used for measurement of D_h by hydrogen chemisorption and that used for isotopic exchange between deuterium and cyclopentane had undergone various modifications since their construction some years ago. It was felt that the time to rationalize the apparatii had come. Therefore, the months of January and February were spent in dissembling the old apparatus and building the new ones.

B. In Situ X-ray Study of Methylcyclopropane Hydrogenolysis

In earlier studies of the catalytic activity of Pt/SiO_2 for this reaction it was noted that some catalysts were much more active after the standard pre-treatment than for a similar pretreatment in which the materials were cooled to reaction temperature in hydrogen rather than helium. This was noted, however, only for two catalysts of lower D_h, 13.8 and 29.3%. A possible interpretation of this is the formation of an inactive or less active hydride phase on the larger Pd crystallites when cooled in hydrogen.

To investigate this matter, in-situ x-ray studies were carried out via flow experiments using the cell shown in Figure 1. The sequence for the measurements is given in Figure 2 and the diffraction peaks at various stages are presented in Figures 3-5 for the catalyst with D_h = 13.8%.

The stored catalyst was first scanned to locate the 2θ position of maximum intensity for the Pd 111 peak. By remaining at that 2θ position and point counting every 10 seconds, any phase transformation of palladium into palladium hydride can be detected by the change in intensity. Hydrogen is then passed over the catalyst and the point counting continued. It is seen in Fig. 6a that the intensity was reduced almost to that of the background within 20 seconds of starting the hydrogen flow. The flow was then switched to helium at the same flow rate. There was a rapid increase in the intensity counts to that of the pure palladium peak but only after 120 seconds, Fg. 6b. The presence of this induction period has also been confirmed at the position of the palladium hydridge 111 peak where the reverse changes occurred. The hydrogen-helium flow cycle was repeated seven times and the results were reproducible. Similar results were also obtained with the catalyst after standard pretreatment. Since the dead space in the copper tubing connecting the reaction system and the in-situ cell was estimated to be 30-40 cc and the flow of hydrogen and helium were both maintained at 180 cc/min, these results suggest that hydride formation is almost instantaneous, however, its removal appears to be autocatalytic. This hysteresis has also been detected in the absorption-desorption isotherm.

After the standard pretreatment of the catalyst, β hydride (∿ 50 pct) was formed during the reaction (hydrogenolysis at 20% conversion) as shown in Fig. 3. However, if the hydride phase is formed during the pretreatment (∿ 90 pct hydride when cooled from 450°C in hydrogen) as shown in Fig. 5, it was not perturbed by the reaction mixture. The hydride formed in both cases, however, could be removed by a short purge of helium either at 25°C or 0°C. Catalyst with $\underline{D}_h$ = 29.3% showed the same trends but less hydride was formed by these treatments (80 pct vs 90 pct). The decrease in activity when hydride forms is perhaps due to the filling of the Pd 'd' band by the 1s electron of the hydrogen or to the formation of a new (bulk d) band structure for the hydride.

During hydrogenolysis, $C_4H_8 + H_2 \rightarrow C_4H_{10}$, hydrogen adsorbs on the surface of the palladium particles to form H* and surface H* reacts with adsorbed C_4H_8 to form C_4H_{10}. The virtual pressure of hydrogen from H* must be less than $\underline{P}_{H2}$ in the gas phase if the hydrogenolysis is to occur at a finite rate. At a particular temperature, the value of the virtual pressure during hydrogenolysis will depend upon the rate constant for adsorption of hydrogen, upon that for reaction of adsorbed hydrogen, and upon $\underline{P}_{H2}$ and $\underline{P}_{C4H8}$. When we start with catalyst in the Pd form, the ratio PdH/Pd was ∿ 0.5 during reaction, although there is some variation in the ratio. From this result, it can be concluded that the virtual pressure of H_2 is slightly less than $\underline{P}_{H2}$. Perhaps the residual Pd consists of those particles of Pd too small to form PdH at the virtual pressure of H_2 in effect, i.e., a large fraction of the metallic area is associated with smaller particles in the Pd form. Of course, the virtual pressure itself may be affected by various kinds of nonuniformity in the palladium particles. However, when we start with catalyst in the PdH form, no PdH is converted to Pd during flow of the hydrogenolysis mixture for 19 min. Apparently, then, there are two steady states depending upon whether the catalyst is initially in the Pd or in the PdH form. Presumably the lack of conversion of PdH to Pd is associated with the induction period observed in the conversion of PdH to Pd in flowing helium. Thus, PdH → Pd would be fast only when the virtual pressure of hydrogen was substantially below the equilibrium value of $\underline{P}_{H2}$.

C. Other X-Ray Characterization Studies

The deuteride has been detected at room temperature in catalysts with D_h = 13.5% and 29.8% treated with D_2 instead of H_2. As with the hydride, a flow of He at room temperature completely reconverts the deuteride to Pd. However, unlike the hydride, the conversion to $PdD_{0.7}$ is essentially 100 pct complete.

II. Pt/SiO_2 Catalysts

A. Hydrogenation of Propylene

A Sequence of turnover frequency measurements was conducted for this reaction at -53°C and $H_2/C_3^=$ of 19/1. The standard pretreatment sequence here was the same as that described in the previous section. In the variable reduction temperature experiments the heating in He to 450°C was omitted and cooling to reaction temperature after reduction was conducted in H_2. These are denoted by VRT(T), where (T) is the temperature of hydrogen pretreatment °C.

Turnover frequencies for the formation of propane at -53°C as a function of percentage exposed (D_h) for standard pretreatment are shown in Figure 7. The hydrogenation reaction is midly structure sensitive with an approximate two-fold change in turnover frequency as D_h changes from 6.3% to 81%. The effect of D_h on turnover frequency is higher at large values of D_h and it levels off at $D_h \simeq 20\%$. Activation energies for four of the catalysts were determined and are given in Table 1. It is apparent that the activation energy for this reaction is independent of the percentage platinum exposed.

TABLE 1

Activation Energies of Pt/SiO$_2$ Catalysts for Propylene;
Standard Hydrogenation Pretreatment Condition

Catalyst	Eact (Kcal/mole
6.3-SiO$_2$-Pt Cl -L	8.95±0.5
40-SiO$_2$-Pt Cl -S	8.44±0.5
63-SiO$_2$-Ion X-S	8.93±0.5
81-SiO$_2$-Ion X-S	8.58±0.5

In previous work we have shown that the structure sensitive behavior of the Pt/SiO$_2$ series was dependent upon the temperature of pretreatment in hydrogen before carrying out the reaction, for both methylcylcopropane hydrogenolysis and deuterium exchange with cyclopentane. A similar study has now been completed for the hydrogenation of propylene. The pretreatments used were the VRT(T) described above with a pretreatment temperature range from -50°C to 450°C.

The results of these pretreatment experiments are shown in Figure 8, representing the turnover frequencies for the formation of propane versus the temperature of reduction. It is evident that the hydrogen pretreatment conditions also have a significant effect on the activity of the Pt/SiO$_2$ series for the hydrogenation of propylene.

An increase is shown for activity of the low dispersion catalysts as the reduction temperature decreases below 200°C. In the temperature range between 200°C and 450°C no effect is shown for any of the catalysts and the activity remains constant. For the highly dispersed catalysts (D_h = 63% and D_h = 81%), there is no significant increase of activity with decreasing the reduction temperature.

The catalyst 21.5-SiO_2-Ion X-L seems to be out of the general pattern of Figure 5 because, even though its dispersion is between that of the 6.3-SiO_2-Pt Cl-L and 40-SiO_2-Pt Cl-S, it does not show a large increase of the turnover frequency at low hydrogen reduction temperatures. Another catalyst similar to the 21.5-SiO_2 -Ion X-L was examined. This catalyst was the 27-SiO_2-Ion X-S prepared by a method similar to that of 21.5-SiO_2 -Ion X-L. The results are shown in Table 2.

TABLE 2

Effect of Reduction Temperature on the Activity for the Catalysts 21.5-SiO_2-Ion X-L and 27-SiO_2-Ion X-S

Catalyst	Pretreatment	N_t, Sec^{-1}
21.5-SiO_2-Ion X-L	VRT (300)	0.071
	VRT (-20)	0.133
27-SiO_2-Ion X-S	VRT (300)	0.101
	VRT (-20)	0.200

From these data it is apparent that both catalysts 21.5-SiO_2-Ion X-L and 27-SiO_2-Ion X-S prepared by ion-exchange are different from the catalysts 6.3-SiO_2-Pt Cl-L and 40-SiO_2-Pt Cl-S prepared by impregnation with H_2PtCl_6. This difference in behavior was not observed for the methylcyclopropane studies.

We wished to know if the rapid increase of the activity for the 6.3-SiO_2 -Pt Cl -L and 40-SiO_2-Pt Cl-S catalysts as the reduction temperature goes down was due to a change in activation energy or due to some other effect.

For this purpose we measured activation energies for D_h = 6.3 after VRT (300) and VRT (-53), and for D_h=81 after VRT (300). The results were 9.7 and 9.6 kcal/mol, respectively, for the former and 10.3 kcal/mol for the latter. Hence it would appear that the nature of the sites active for propylene hydrogenation is independent of pretreat temperature and platinum particle size and that the increase in activity for some of the catalysts at low reduction temperatures is the effect of changing the number of active sites rather than their nature.

We have now completed in situ x-ray studies of the effect of the temperature of H_2 reduction on the mean-square amplitude of vibration of Pt atoms in these catalysts. This amplitude increases by ∿50 pct as the temperature of the reduction is increased from room temperature to 450°C. We are now attempting to correlate these changes with the alterations in structure sensitivity.

B. Other X-Ray Studies

Earlier we had reported that only for D_h = 6.7 pct, increasing the temperature of He reduction as in room temperature to 450°C, caused an irreversible decrease of ≃30 pct. in the amount of Pt present, as determined from the area of the diffraction profiles. We have now completed studies of the Pt fluorescent x-ray intensity (produced by Mo$k\alpha$) after such treatments. The results show that the Pt is all still present, so that either some of it dissolves in to support, or the Pt particles have been broken down to a very fine size by the pre-treatment (perhaps even becoming amorphous). If the latter is the case, there will be a large increase in small-angle x-ray scattering, and such a study is now under way.

We have continued our attempts to elucidate the structure of the most highly dispersed catalysts with synchrotron radiation to obtain adequate intensity. Our equipment at the Cornell CESR storage ring has been improved and we have finished software for control and data taking, and, as well, a portable gas train. However, the intensities we obtain are only ∿ 15 times those we see "at home," with our rotating anode unit. Therefore, we have embarked on some development to improve this by an order of magnitude, by trying different monochromator crystals. A two week run is schedule in April.

WORK PROJECTED FOR THE PERIOD 1 MARCH TO 30 JUNE, 1981

1) Improvement of intensity obtained in experiments at the Cornell CESR storage ring.

2) Construction of a modified in situ x-ray cell to be used for in situ studies of propylene hydrogenation. The present cell design must be altered since the hydrogenation proceeds at reasonable rates at temperatures much lower than the hydrogenolysis.

3) Initiation of pretreatment-structure sensitivity studies of propylene hydrogenation on the Pd/SiO_2 series.

4) Initiation of controlled atmosphere x-ray studies of Pd/SiO_2 after various treatments as done for Pt/SiO_2.

EFFORT DEVOTED TO THIS PROJECT

During the academic year (8 months to date during the term of the present contract) each co-principal investigator has spent 8 pct. of his time on this project. Summer effort was 100 pct. for 1/2 month for Prof. Butt and one month for Prof. Burwell. The 8 pct. effort will be continued until 30 June 1981. A full time graduate research assistant, Mr. Elias Rorris, has been associated with the project during the entire term of the present contract (with Prof. J. Butt).

Dr. R. Nandi continues as a postdoctoral fellow with Prof. Cohen and Dr. R. Pitchai with Prof. Burwell.

Publications and Activities

Burwell:

"Isotopic Exchange between Alkanes and Deuterium on Activated $Mo(CO)_6/Al_2O_3$," Seventh International Congress on Catalysis, 1980, in press, C. Defosse, M. Laniecki, and R. L. Burwell, Jr.

"Surface Induced Alkyl Migration Reactions in Metal Carbonyls" J. Am. Chem. Soc., 102, 5112 (1980), F. Correa, R. Nakamura, R. E. Stimson, R. L. Burwell, Jr., and D. F. Shriver.

"Molybdenum(0)/Dehydroxylated Alumina Catalysts," J. Am. Chem. Soc., 103, Jan. (1981), R. Nakamura, R. G. Bowman, and R. L. Burwell, Jr.

"Catalytic Activity of Supported f-Element Organometallic Complexes," J.C.S. Chem. Comm., 1981, in press, R. G. Bowman, R. Nakamura, P. J. Fagan, R. L. Burwell, Jr. and T. J. Marks.

"Catalysts Derived from $Mo(CO)_6/Al_2O_3$," Accts. Chem. Research, submitted, R. L. Burwell, Jr.

Butt:

"Catalyst Poisoning and Chemical Process Dynamics" Proc. First Int. Symposium on Catalyst Deactivation, Antwerp, Belgium, October 13-15, 1980. Elsevier, Amsterdam (1980). Vol. 6, Studies on Surface Science & Catalysis.

"Modification of the Structure Sensitivity of Supported Pt Catalysts," Proc. 7th Iberoamerican Symposium on Catalysis, LaPlata, Argentina, July 13-18, 1980.

"Kinetic Separability of Catalyst Poisoning," Proc. 7th International Congress on Catalysis, Tokyo, Japan, June 30-July 4, 1980. (With I. Onal).

"Catalyst Poisoning and Fixed Bed Reactor Dynamics; The Startup and Quasi-Steady State. Profiles in Fresh and Deactivated Fixed Bed Adiabatic Beds," The Chem. Eng. Journal (with R. M. Billimoria).

"Particle Size Determination in Supported α-Fe_2O_3", (with J. A. Amelse, K. B. Arcuri, R. J. Matyi, L. H. Schwartz and A. Shapiro), J. Phys. Chem., in press.

"Iron Alloy Fischer-Tropsch Catalysts, Part III. Conversion Dependence of Activity and Selectivity," (with J. A. Amelse and L. H. Schwartz) J. Catalysis, submitted.

Cohen:

M. R. James and J. B. Cohen, "The Measurement of Residual Stresses by X-ray Diffraction Techniques," "Trestise on Materials Science & Technology," Vol. 19A, (1980) Academic Press, Inc. New York, 62 pp.

M. Morinaga, J. B. Cohen and J. E. Faber, Jr., "X-ray Diffraction Study of $(ZrCa,Y)O_{2-x}$" Part II: "Local Ionic Arrangements" Acta Cryst. A36, 520-530 (1980).

E. Gartstein & J. B. Cohen, "Comments on the Defect Structure in Wustite," J. Solid State Chemistry, 33, 271-72 (1980).

M. Morinaga and J. B. Cohen, "The Defect Structure of VOX - Comparison Between X-ray and Electron-Diffraction," Acta Cryst. A36 1070-71 (1980).

J. B. Cohen, J. Faber and M. Morinaga, "The Structure of Disordered Stabilized Zirconias," J. Of Ionics, in press.

J. B. Cohen, "Local Order," Encyclopaedia of Materials Science, in press.

P. Georgopoulos and J. B. Cohen, "The Defect Arrangement of Non-Stoichiometric β'NiAl," Acta Met. in press.

J. B. Cohen, J. Faber and M. Morinaga, "The Structure of Stabilized Zirionias," J. of Ionics, in press.

Accepted Paper Dealing with this Research

"In-Situ X-Ray Diffraction Studies During Treatment and Hydrogenolysis: Pd/SiO_2, I." (With R. K. Nandi, R. Pitchai, S. S. Wong, J. B. Cohen and R. L. Burwell, Jr.) J. Catalysis, in press.

Lectures and Presentations

Seminars and lectures dealing with various aspects of this research were presented as follows:

Burwell:

University of Cairo, Egypt, November 1980.
University of Wisconsin, Milwaukee, January 1981.

Butt:

7th Iberoamerican Symposium on Catalysis, La Plata, Argentina, July 1980.
Imperial College, London, England, October 1980.
General Electric Company, Schenectady, N.Y., November 1980.
Ashland Oil Co., Ashland, Ky., January 1981.

Cohen:

American Crystallographic Association Meeting, Lubbock, Texas, March 1981.

Nandi:

Second North American Chemical Congress, Las Vegas, Nevada, August 1980.

Figure Captions

Figure 1 Cell for diffraction studies during hydrogenolysis: a, g - teflon needle valve, b, f - glass wool, c - pretreatment section, d, - rotoflow valve for inserting catalyst in the cell, e - reaction region.

Figure 2 Flow chart for studies of the effects of different treatments and of methylcyclopropane hydrogenolysis upon the diffraction pattern of $\underline{D}_h$ - 13.8% Pd/SiO_2. Rectangular boxes indicate that the sample was examined by x-ray diffraction. The step scanning procedure was employed except where point counting is indicated. Roman numerals represent the x-ray scans shown in Figs. 3-5; t is the time in minutes at which the scans were made. The ratios below the boxes represent the proportions of Pd and PdH_x formed.

Figure 3 Diffraction profiles at various stages (I-IV) in Fig. 2, starting with stored catalyst. MCP - methylcyclopropane.

Figure 4 Diffraction profiles at various stages (V-VIII) in Fig. 2.

Figure 5 Diffraction profiles at various stages (IX-XII) in Fig. 2, starting with β $PdH_{0.7}$.

Figure 6 Intensity in CPS vs time for (a) formation and (b) decomposition of hydride at 25°C measured at the 111 peak maximum. Stored Pd/SiO_2 of $\underline{D}_h$ = 13.8% had been exposed to these cycles like those of Fig. 5 before t = 0 min.

Figure 7 Turnover Frequency vs. Percentage Exposed for Propylene Hydrogenation at -53°C after Standard Pretreatment; Pt/SiO_2.

Figure 8 Effect of Reduction Temperature on the Hydrogenation of Propylene; Pt/SiO_2.

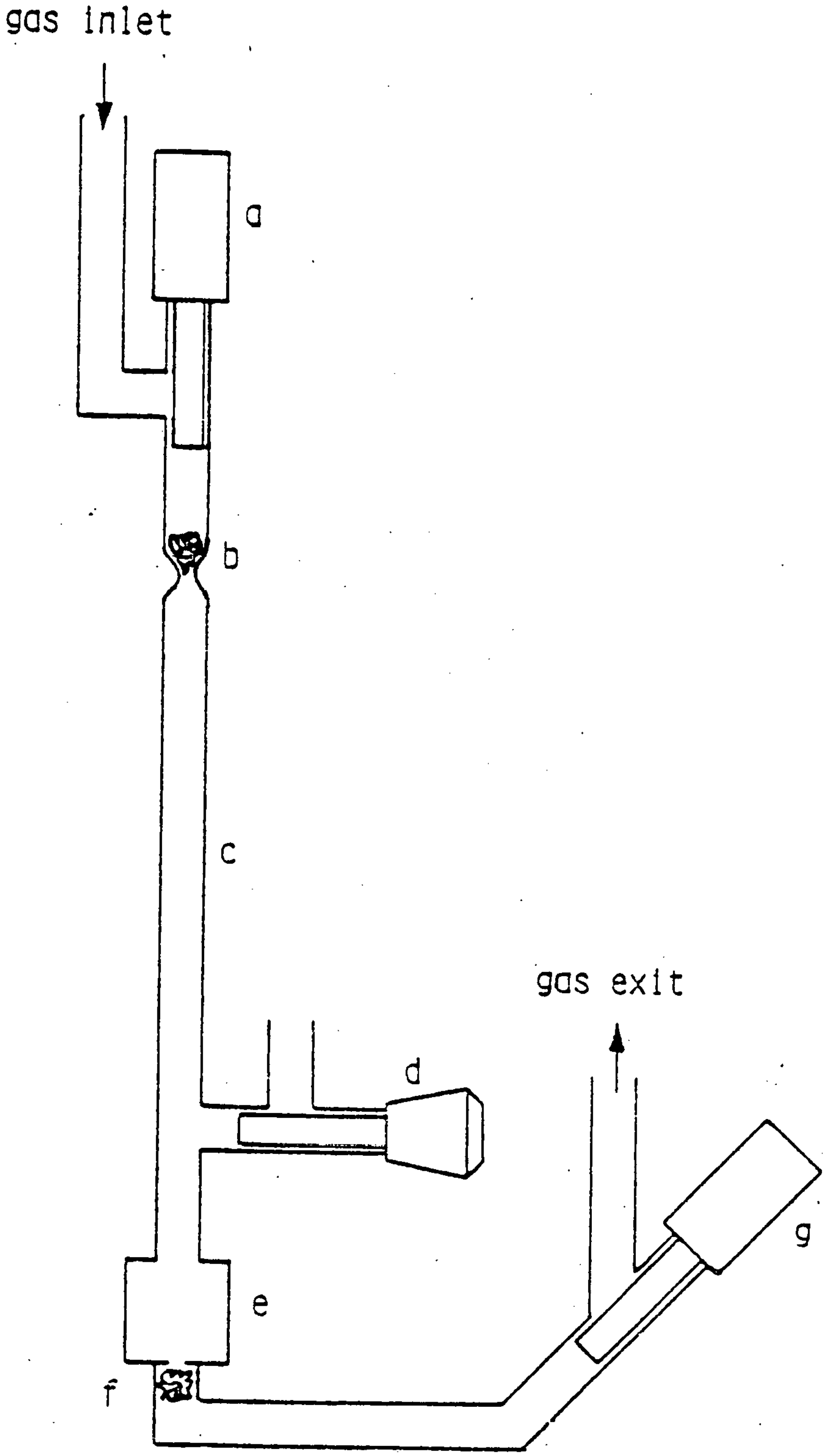

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Fig. 1

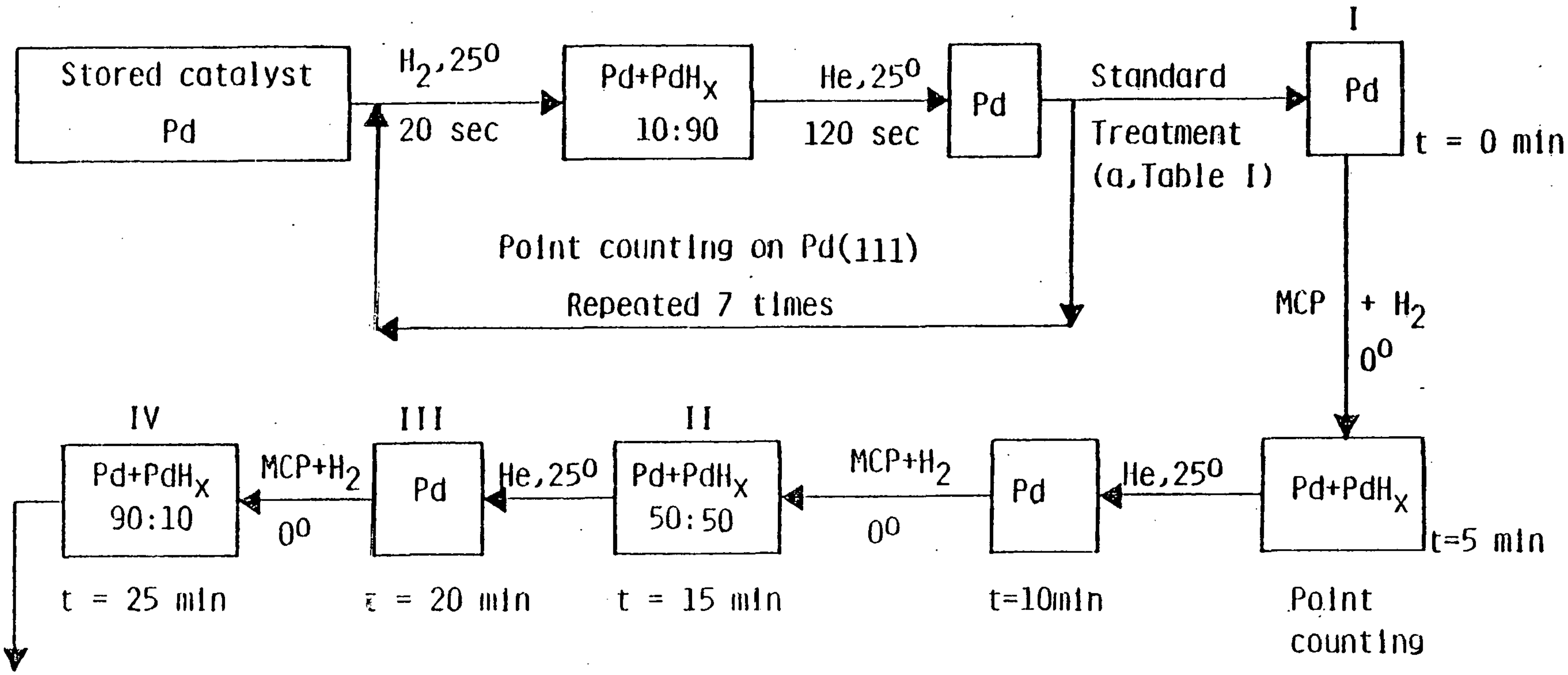

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Fig. 2

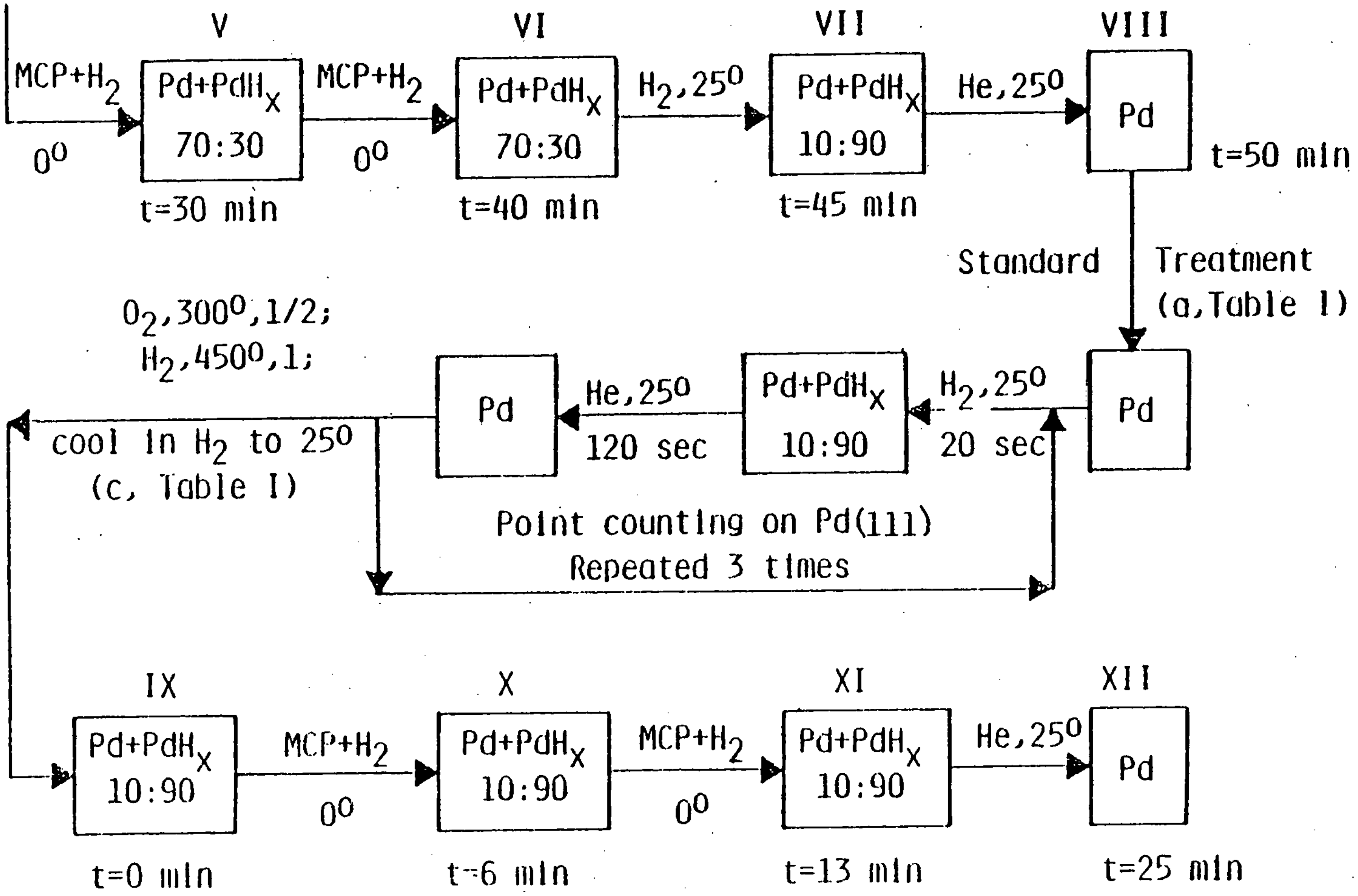

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Fig. 2 (cont'd)

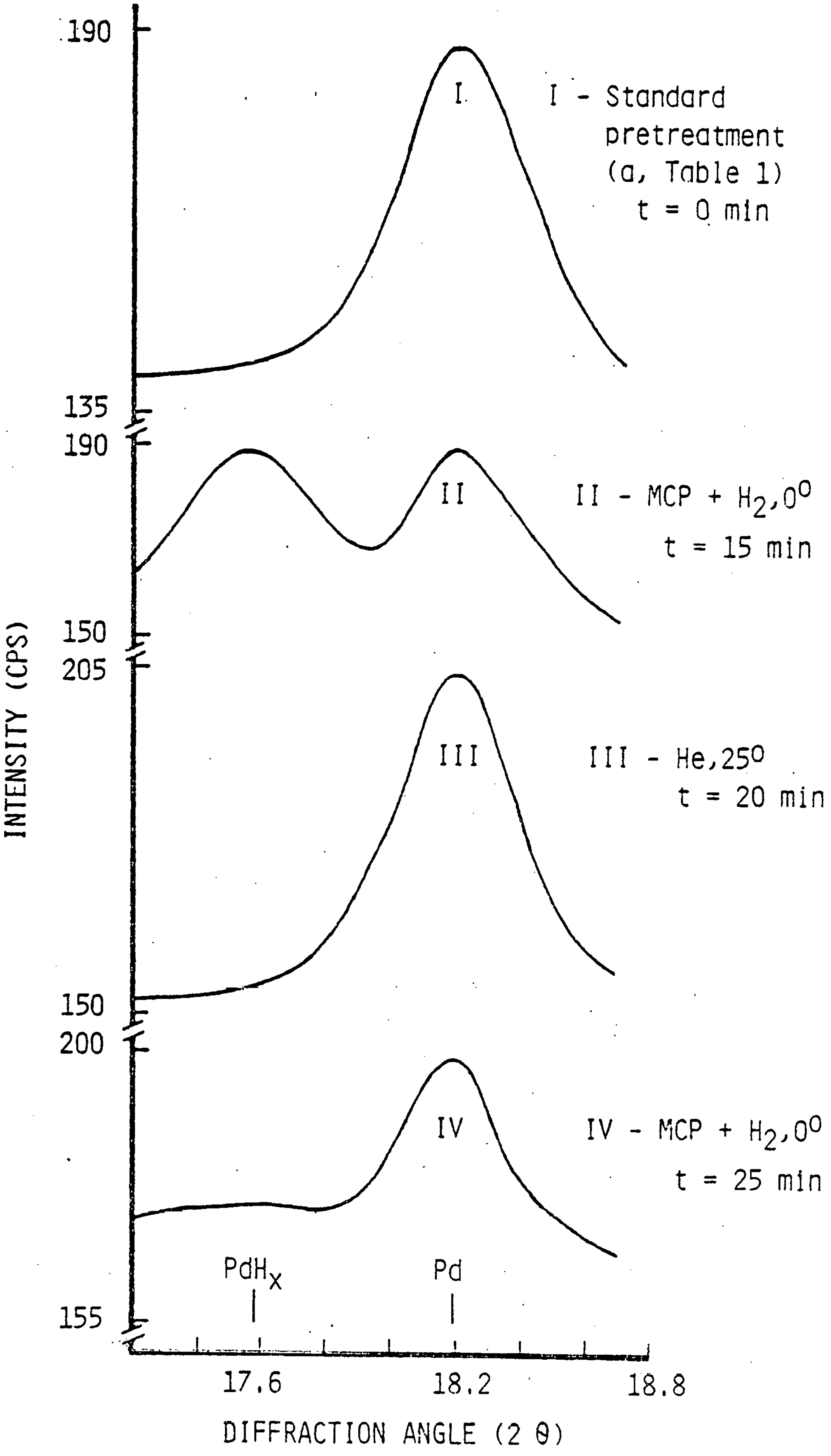
190
135
190
150
205
150
200
155
INTENSITY (CPS)
I
I - Standard pretreatment (a, Table 1) t = 0 min
II
II - MCP + H2,0°
t = 15 min
III
III - He,25°
t = 20 min
IV
IV - MCP + H2,0°
t = 25 min
PdHx
Pd
17.6
18.2
18.8
DIFFRACTION ANGLE (2 θ)

Fig. 3

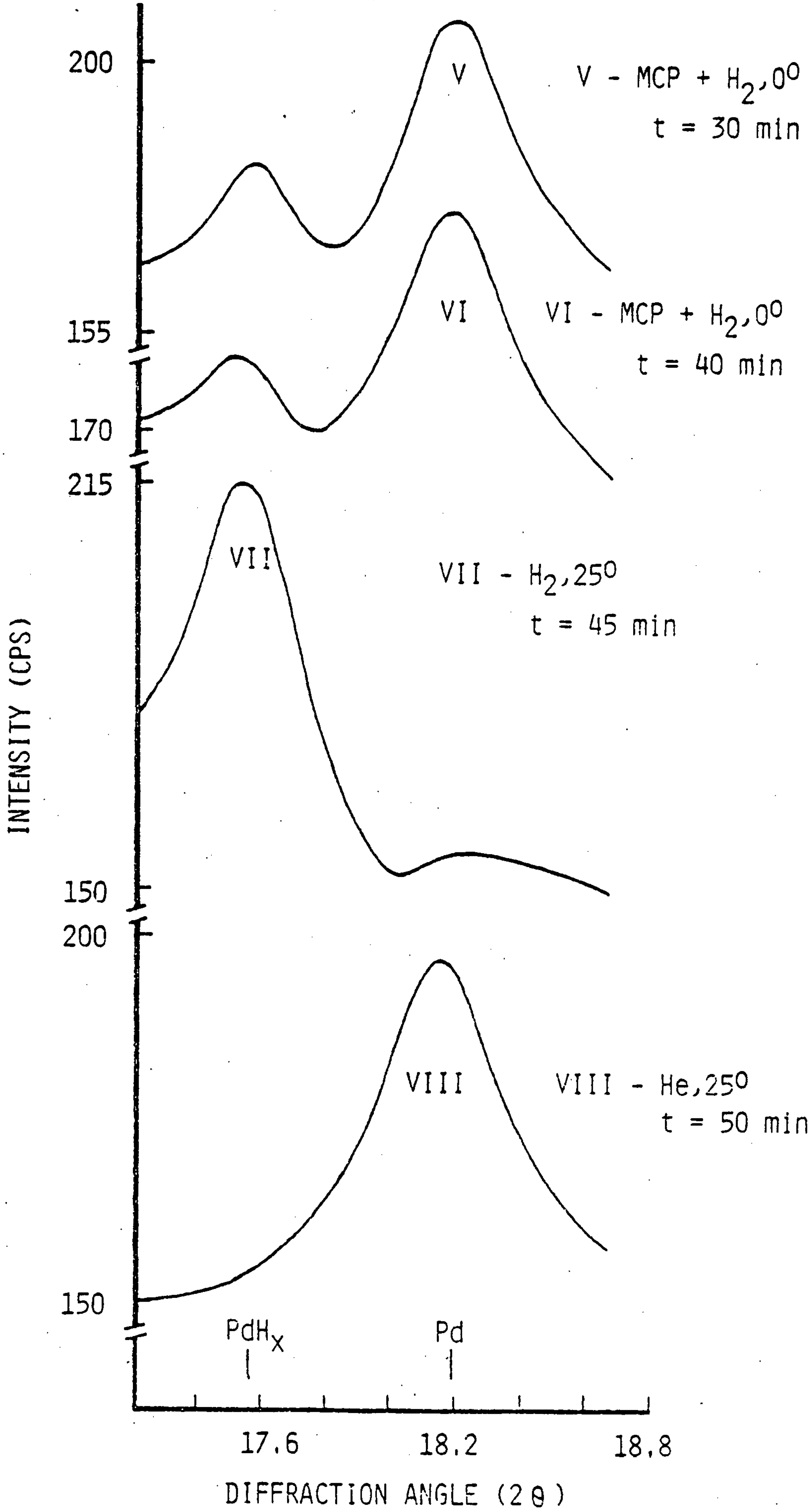

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Fig. 4

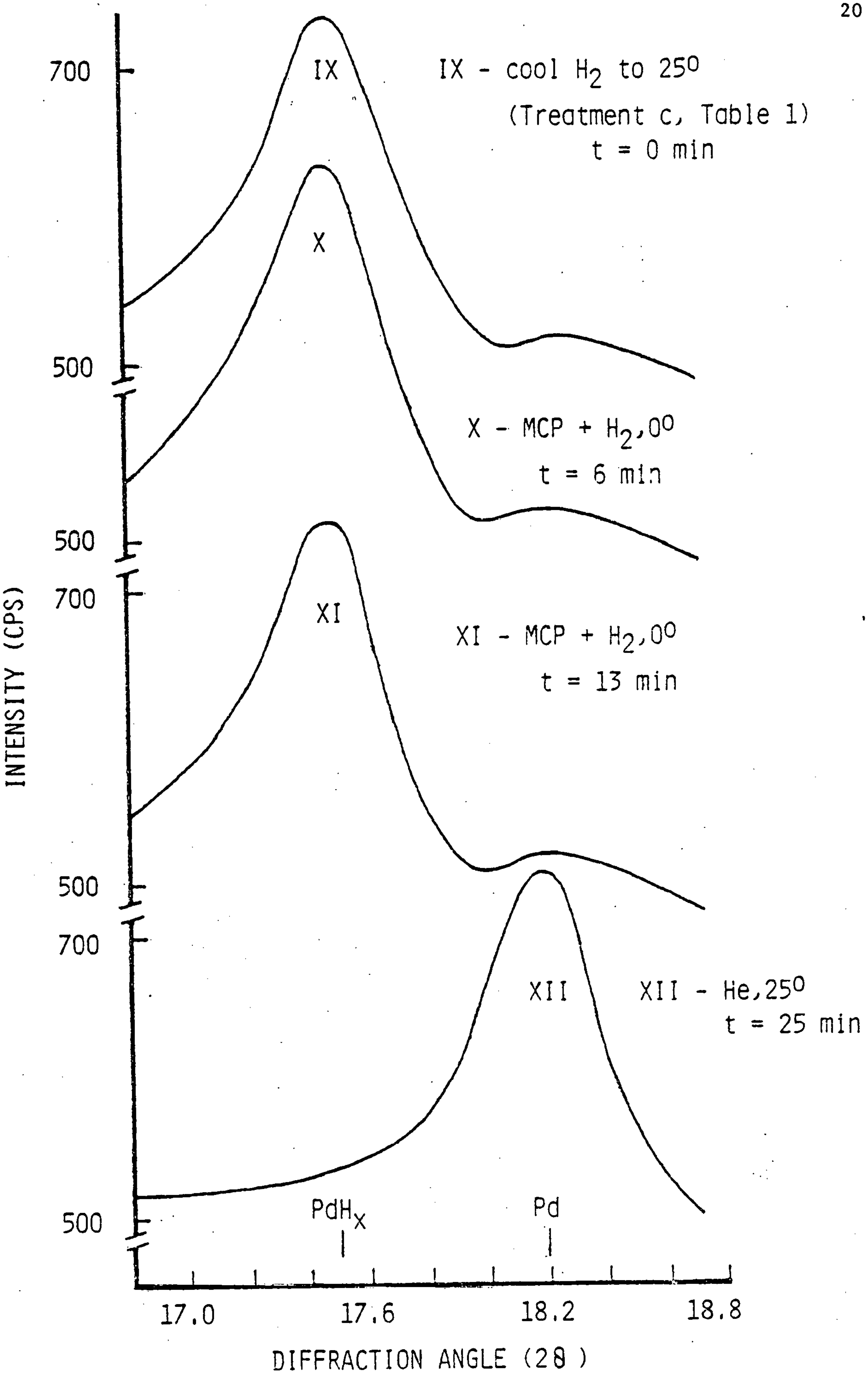
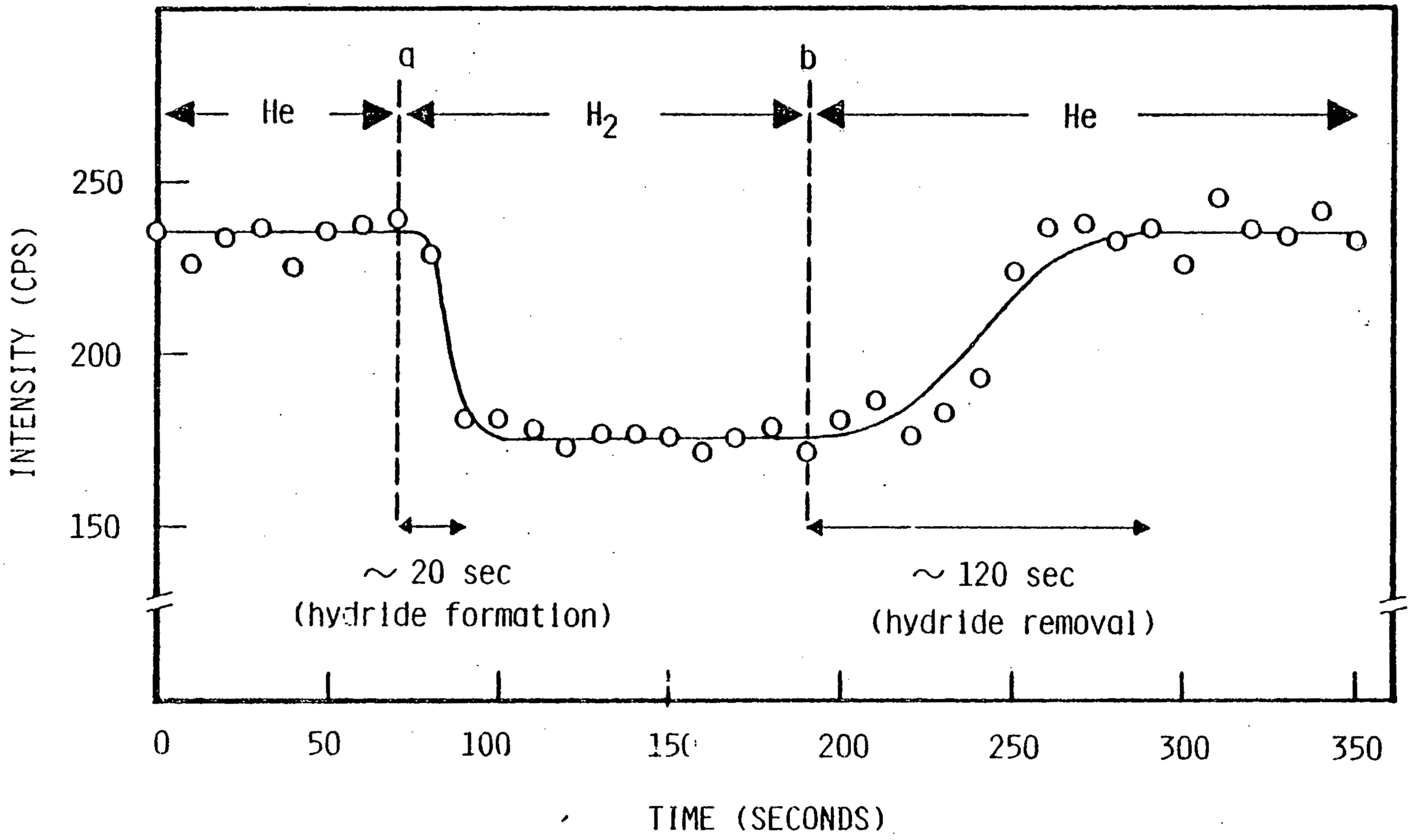

700
IX
IX - cool H_2 to 25°
(Treatment c, Table 1)
t = 0 min
X
500
X - MCP + H_2, 0°
t = 6 min
500
700
XI
XI - MCP + H_2, 0°
t = 13 min
500
700
XII
XII - He, 25°
t = 25 min
500
INTENSITY (CPS)
PdH_x
Pd
17.0
17.6
18.2
18.8
DIFFRACTION ANGLE (2θ)

Fig.5



Nandi et al.

Fig. 6

FIGURE 7.

N_T vs. Percentage Exposed at Standard Pretreatment Condition.

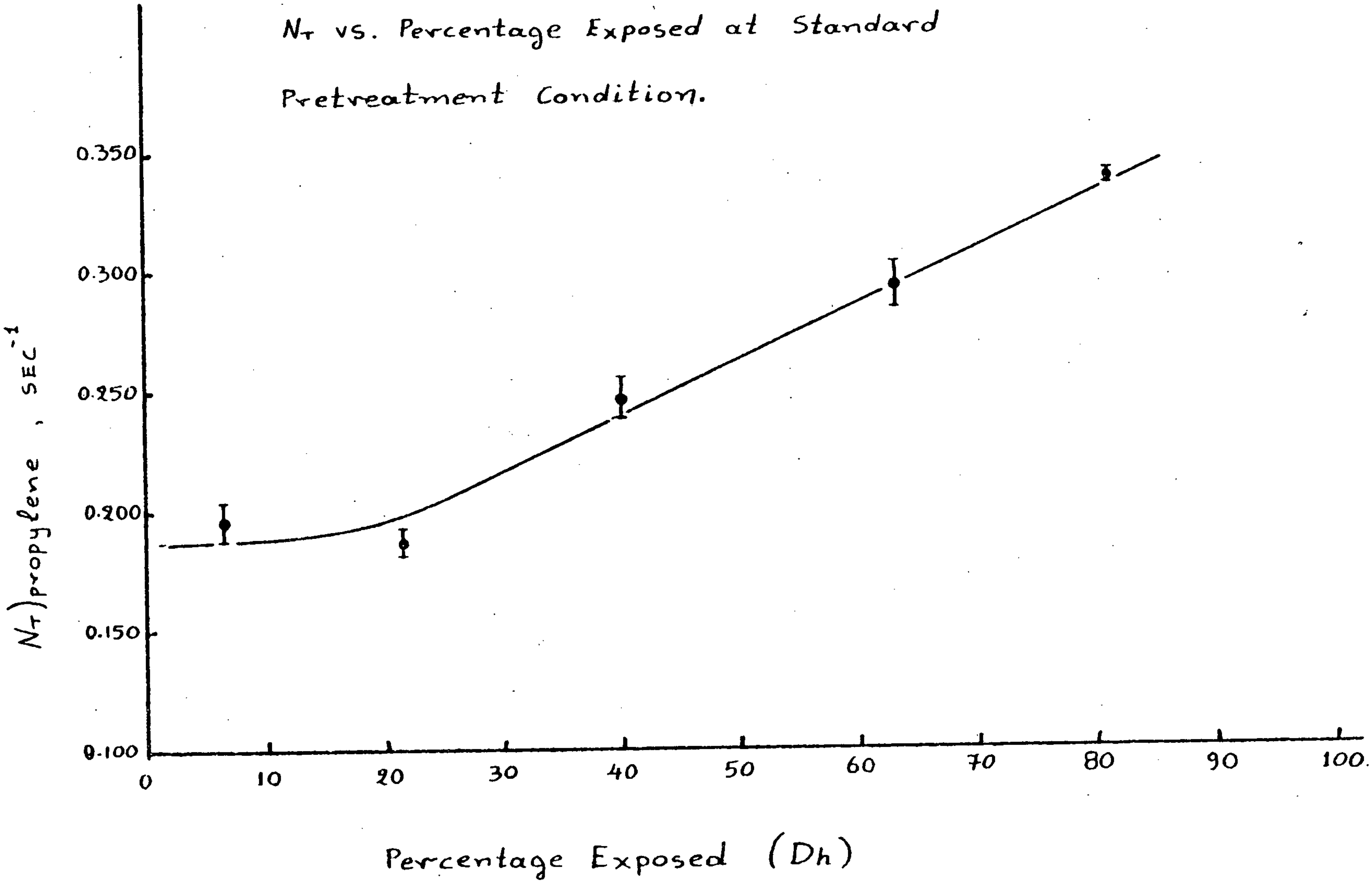
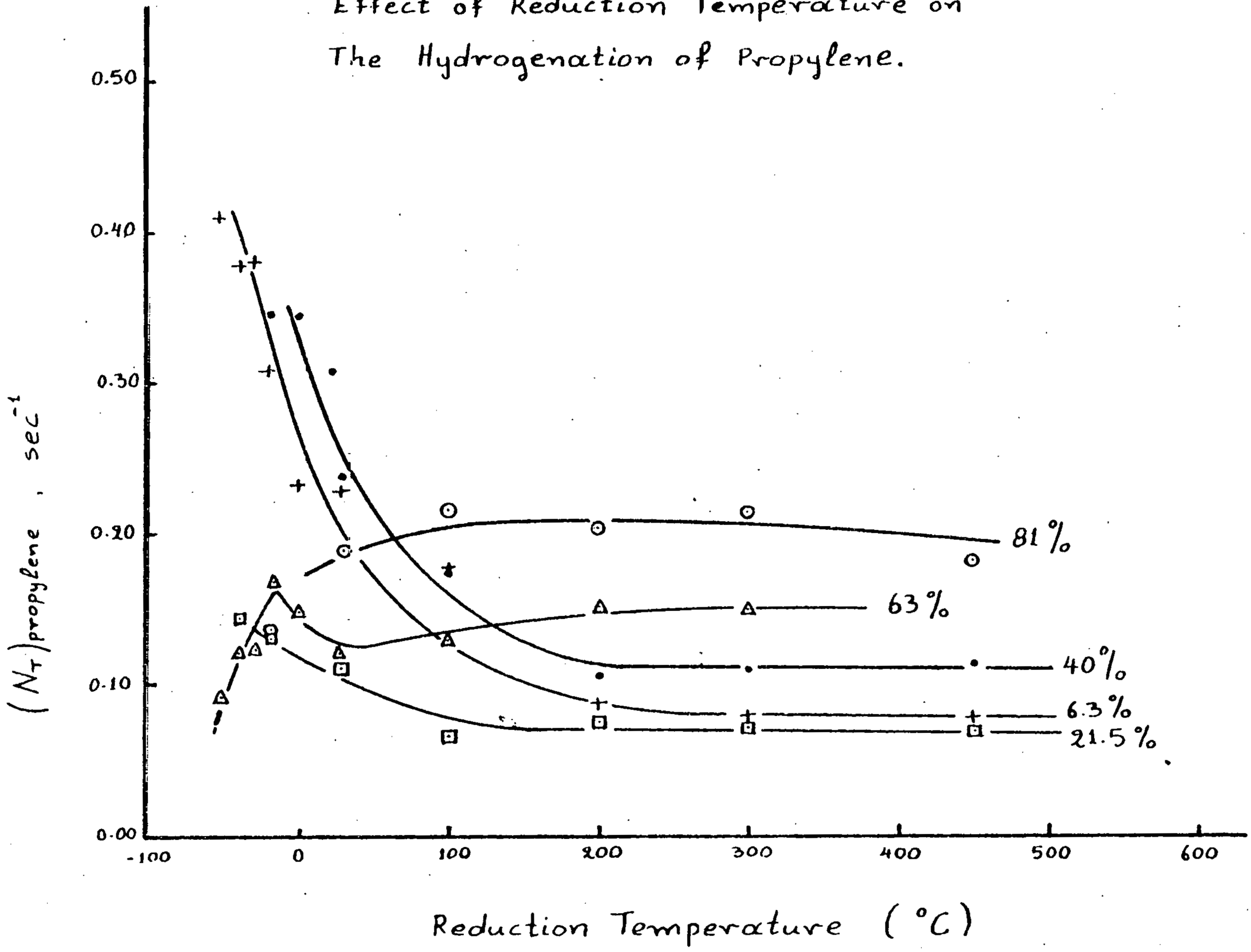


FIGURE 8.

Effect of Reduction Temperature on The Hydrogenation of Propylene.



Item 2 of 4

Financial Statement of Estimated Costs

Northwestern University

Contract DE-AC02-77ER04254

1.	Estimated Total Project Costs for the Current Period	$90,000	
2.	Total Amount Chargable to DOE		$90,000
3.	Cumulative Support Costs		271,000
4.	Estimated Total Cumulative Support Costs		361,000
5.	Cumulative Support Ceiling		361,000
6.	Anticipated Difference Between Item 4 and Item 5		-0-