Item 1 of 4

MASTER

Report COO-4254-3

Progress Report

"The Properties of Supported Metal Catalysts"

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Report for the Period 4/1/79 - 4/1/80

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Abstract

Some eleven Pd/SiO_2 catalysts have been prepared by ion exchange or impregnation, with percent exposed varying from 7.3 to 82.8. This percent exposed has been measured by hydrogen chemisorption at 60° C, at which temperature there is good agreement with X-ray diffraction. Stored catalyst is more difficult to reduce than clean catalyst with short-time exposure to oxygen. Oxidation is less complete as percent exposed decreases. Upon cooling in H_2 from 450° C and flushing with Argon, there is more H than in a catalyst exposed to H_2 at 25° C and then flushed. The Pd particles are more elongated then the Pt catalysts we have studied, and the particles are less perfect.

The activity and selectivity of the entire series was examined with the hydrogenolysis of methyl cyclopropane at 0° C. These catalysts are mildly structure sensitive. Formation of palladium hydride during pretreatment (observed with in-situ x-ray diffraction studies) reduces the activity, but this occurs primarily for the low dispersions. Purging in O_2 He or Ar for 15-30 min. at 20°C eliminates the hydride. The turnover frequency for i-butane formation is ten times higher for Pt/SiO_2 than for these Pd/SiO_2 catalysts, but the n-butane activity is similar for both; as a result the selectivity of Pd/SiO_2 is one sixth that for the Pt/SiO_2 catalysts.

The reduction in loading with increasing temperature of H_2 reduction of Pt/SiO_2 (reported in the last summary) has been confirmed with additional x-ray measurements and by desorption studies. This effect is largest for the lowest pct. exposed, and is accompanied by a decrease in particle size and a shift of the size distribution to smaller sizes.

WORK ACCOMPLISHED SINCE LAST REPORT TO 1 MARCH 1980

I. Pd/SiO_2 Catalysts

A. Preparation

As with the Pt/SiO_2 catalysts previously studied, we wanted to avoid any temperature over 450°C during preparation. This done, the silica surfaces of all catalysts would be identical after the standard pretreatment which ends with flushing with argon at 450°C. We also wished to avoid complications which might arise from the presence of chloride ion. Accordingly, the Pd/SiO_2 catalysts were made by ion exchange of Davison Grade 62 silica gel with $Pd(NH_3)_4(NO_3)_2$ followed by reduction. Catalysts with percentages exposed, $\underline{D}_h$, of about 80% resulted if well dried $Pd(NH_3)_4^{2+}/SiO_2$ was reduced in H_2. However, unlike the analogous case with $Pt(NH_3)_4^{2+}/SiO_2$, preliminary calcination at up to 450°C followed by reduction gave about the same D_h rather than drastically reduced D_h. We found that reduction with wet hydrogen led to reduced values of D_h as was the case for Pt/Al_2O_3. To avoid concentration gradients of water in a catalyst bed, reduction was carried out in a fluidized unit. The following catalysts were then prepared. (The catalyst designation starts with D_h in percent.)

Catalyst	Pd, %	Designation
A	0.51	82.8-SiO_2-PdIonX
I	0.49	79.1-SiO_2-PdIonX
B	0.51	68.1-SiO_2-PdIonX
F	1.56	65.8-SiO_2-PdIonX
H	2.09	65.5-SiO_2-PdIonX
G	1.56	49.8-SiO_2-PdIonX
L	2.09	29.3-SiO_2-PdIonX
K	2.09	19.8-SiO_2-PdIonX
J	2.09	13.8-SiO_2-PdIonX
D	1.52	22.5-SiO_2-Pdacac
C	1.52	7.3-SiO_2-Pdacac

The last two catalysts were prepared by impregnation with $Pd(acac)_2$ (acac = acetylacetone minus one atom of H) in an attempt to get low D_h. These catalysts behaved anomalously and exhibited lower activities than the other catalysts. The anomaly was not corrected by oxidation at 450°C rather than the 300°C of the usual pretreatment. We have made a number of attempts to prepare $Pd-SiO_2$ catalysts with $D_h > 80\%$. So far we have been unsuccessful.

Because of possible formation of bulk palladium hydride, measurement of D_h by hydrogen chemisorption posed problems. One needed to be sure that adsorption alone was measured without contribution from absorption. Initially we ran chemisorptions at 60°C with D_2 rather than H_2 since bulk palladium deuteride is less stable than the hydride. However, problems arose in desorption in argon to 450°C. The adsorbed D atoms exchanged with surface hydroxyl groups on the silica gel and the desorbed gas was largely H_2. Differences between the thermal conductivities of H_2 and D_2 made measurement of adsorption impossible. We then switched to measuring chemisorption of H_2 at 60°C and established that this led to no problems. Any bulk PdH which was formed, rapidly decomposed in flowing argon when the surface of the palladium was free of oxide.

As with Pt/SiO_2 and Pt/Al_2O_3, the apparent value of D_h depends upon the temperature of hydrogen chemisorption. D_h measured at 100°C was 81% of that measured at 25°C for 82.8-SiO_2-PdIonX, 83% for 49.8-SiO_2-PdIonX, and 75% for 13.8-SiO_2-PdIonX. There is no a priori evidence as to what temperature of chemisorption gives the best approach to H/Pd_s being unity. In principle, all of the values of D_h in the table of catalysts might be too high or too low by some factor. However, our X-ray results are in good agreement with the results in the table, which supports our choice of a temperature of 60°C.

Some studies of the oxidation of Pd/SiO_2 followed by reduction in hydrogen were made. The amount of oxygen adsorbed from 5 pulses of O_2 at 25°C was measured on all of the catalysts in the Table. In all cases, O/Pd_s was near 0.83. The adsorbed oxygen was removed by pulses of hydrogen at 60°C. If the catalysts were exposed to O_2 at 25°C for 0.25 hr, 5 pulses of H_2 at 60°C fully removed the adsorbed oxygen but removal was not very fast and some reaction with oxygen occurred even in the 5th pulse. Exposure of clean catalyst to O_2 at 100°C for 1 hr led to a ratio O/Pd_s of very nearly unity. The oxygen was entirely removed by pulses of H_2 at 100°C.

In our pretreatments, stored catalyst is first exposed to O_2 at 300°C for 1/2 hr and then reduced by H_2 at various temperatures. Reduction by hydrogen at 25°C for 1 hr was incomplete for oxidized Pt/SiO_2, but oxidized Pd/SiO_2 was fully reduced in all cases. Oxidation by O_2 at 300°C for 3 hr completely oxidized 79.1-SiO_2-PdIonX to PdO but oxidation became increasingly incomplete as one went to smaller D_h (larger particles of Pd). Such oxidized catalysts appeared to have an oxide layer over a metallic core.

A Pd/SiO_2 catalyst cooled in H_2 from 450°C and flushed with Ar at 25°C contains 14% more H than a catalyst first exposed to H_2 at 25°C and then flushed with Ar. We currently do not know where the extra hydrogen is located.

B. Chemical Reactivity

The hydrogenolysis activity and selectivity of the series of silica supported palladium catalysts was studied as a function of percentage metal exposed and pretreatment conditions.

The hydrogenolysis reaction is carried out at 0°C with a hydrogen to methylcyclopropane ratio of 16: 1 in a differential reactor flow system. Turnover frequencies for the major product, i-butane, for the standard pretreatment condition (O_2, 300°C, 0.h; H_2, 300°C, h; He, 450°C, h; cool in He) are shown in Figure 1 and the corresponding selectivity (i-butane/n-butane ratio) is shown in Figure 2. The increase in activity is clearly beyond the range of experimental uncertainties so the reaction is mildly structure over the series of catalysts. Whether the activity really passes through a maximum around a D_h value of 65% requires further investigation.

Formation of palladium hydride during the pretreatment of the catalyst reduces the activity of the catalyst and this effect is shown to be structure sensitive. Turnover frequencies for i-butane formation are shown in Figure 3 for the pretreatment O_2, 300°C, 0.h; H_2, 450°C, h; cool in either He or H_2. The series of catalysts showed the same pattern for the structure sensitivity as the standard pretreatment; however, catalysts of low D_h showed lower activity when cooled in hydrogen as compared to those colled in He. X-ray diffraction studies of low D_h catalysts after the treatment involving cooling in hydrogen, showed the formation of palladium hydride (with about the same particle size as the Pd) in the catalyst, with 80-90% of the metal transformed into the hydride phase. As the percentage exposed of the catalysts increases, differences between cooling in H_2 and cooling in He become negligible in terms of reactivity. This is now being examined in-situ with diffraction to see if this means that there is no hydride produced when the higher D_h catalysts are cooled in hydrogen.

We have also found with x-rays that purging in O_2 or He at room temperature for 15-30 minutes eliminates the hydride. (The x-ray studies described here are being carried out in our in-situ system described in the previous report, and with a rotating anode generator.)

The effect of different hydrogen pre-treatment conditions on the activity and selectivity for methylcyclopropane hydrogenolysis is very small as compared to that for the series of Pt/SiO_2 and Pt/Al_2O_3 catalysts reported previously. The i-butane turnover frequency decreases by about 30% when the reduction temperature is varied from 25° to 450°C; however, the n-butane activity remains essentially constant. Summaries of the structure sensitivity for the reaction at different pre-treatment conditions are given in Figures 4 and 5. As shown in these Figures, the patterns for the structure sensitivity did not change with different pre-treatment conditions.

Comparison with the results previously obtained with a series of Pt/SiO_2 catalysts reveals the turnover frequency for i-butane formation to be ten times higher for the Pt/SiO_2 catalysts than for Pd/SiO_2, but the n-butane activity is about the same for both. The corresponding selectivity is about six times higher for the Pt/SiO_2 catalysts due to the high i-butane activity compared to Pd/SiO_2.

C. Additional X-ray Studies

Many of our x-ray results have already been mentioned in the previous sections. But also: The Pd catalysts differ from the Pt ones we have prepared in that the particles are not equiaxed but elongated in shape. Furthermore, there are microstrains present (detected by Fourier analysis of peak shape) at least up to D_h = 29.3 pct.; the Pd particles are not as perfect as the Pt ones.

D. Work Projected for the Period 1 March to 30 June 1980.

1) In-situ x-ray studies will continue, with three goals in mind:

a) Does hydride form in the high D_h catalysts? The reactivity studies indicate that the answer is no. (Fig. 3), but it is important to be sure of this.

b) Does hydride form in the presence of the hydrocarbon? A special cell has been constructed to examine this so that we can duplicate the flow conditions in the reactivity studies.

c) Is hydride as easy to form and remove in stored catalysts as it is in freshly calcined product, especially for small D_h.

2) We will prepare and characterize Pd/SiO_2 catalysts made by reaction

of silica gel with Pd (Π-allyl)$_2$, by the method of Ermakov. Such catalysts are of current interest and they have been reported to have very large values of D_h.

3) The isotopic exchange between D_2 and cyclopentane will be examined, in the same way as previously reported for Pt/SiO$_2$ and Pt/Al$_2$O$_3$.

4) If we succeed in making high D_h catalysts (> 75 pct.), their activity and selectivity (in methyl-cyclopropane hydrogenolysis) will be measured.

II. Pt/SiO$_2$ Catalysts

A. X-ray Studies

In the last report we described our finding that the pct. loading drops considerably and irreversibly as the temperature of H_2 reduction increases from 25°C. This affect was detected from our in-situ x-ray measurements. We have since repeated these x-ray measurements several times with the same result. This effect is largest for the lowest D_h catalyst, (6.3-SiO$_2$-PtCl-L) for which a 25 pct. reduction in loading was observed. At the same time the particle size is reduced from ~ 102 Å to 92 Å, and the particle size distribution shifts to smaller sizes as shown in Fig. 6. These effects have now also been detected with H_2 desorption; a H_2 reduction at 450°C leads to an apparent D_h of only 4 pct. and subsequent exposure of the catalyst to the standard pretreatment does not restore D_h to its normal value of 6.3 pct. If the effects seen with x-rays were due to a size reduction, then the D_h value should have been <u>higher</u>. Instead, it is <u>lower</u>. At this point we do not know if some intermediate Pt compound is vaporizing, or if H_2 is disordering the surface or if Pt is dissolving in the gel. If the H_2 was disordering surface layers, the effect would increase with increasing D_h, but we see no such effect with the higher D_h catalysts. Particle size, shape and distribution (all now measured with x-rays in-situ) are unaffected by the temperature of H_2 treatment for the higher D_h, see Fig. 7. We plan to measure total Pt x-ray fluorescence before and after such a treatment. If there is no loss in Pt, then solution would seem to be indicated.

It is interesting to note the differences in the size distributions in Fig. 6 and 7. For the lower D_h catalyst, the distribution tails to small sizes, but the reverse is true for larger D_h. Also, for the $D_h = 6.3$ % catalyst, the microstrains present after preparation are unaffected by H_2 treatment. (As we have reported before, all other catalysts are strain-free.)

B. Work Projected for the Period 1 March to 30 June 1980.

1) Our measurements of lattice parameter and mean-square-amplitude of vibration for various D_h, in various gas atmospheres is nearly complete already, and will be so before 30 June.

2) The fluorescence studies mentioned above will be carried out.

3) Our diffractometer is completely set up at Cornell University's synchrotron, and we have developed a carrier for our catalysts, to maintain them in appropriate gas atmospheres while moving them from Northwestern to Cornell. We expect to make our first examinations of the high D_h Pt and Pd catalysts ($\approx$ 80 pct.) during April or May. (We had originally planned to do this last summer, but Cornell has had its own problems! Experiments there will only just start in the next few weeks.)

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 one month for both Profs. Butt and Burwell. The 8 pct. effort will be continued until 30 June 1979. A full time graduate research assistant, Mr. Steven Wong, has been associated with the project during the entire term of the present contract (with Prof. J. Butt)

Dr. R. Nandi was a postdoctoral fellow for the entire period (with Prof. J. Cohen), Dr. R. Pitchai joined the project 18 August 1979 (with Prof. Burwell).

Publications and Other Activities

1) Publications

"The Role of Carbonaceous Deposits in the Hydrogenation of Hydrocarbon on Platinum Catalysts," T. Hattori and R. L. Burwell, Jr., J. Phys. Chem., 83, 241 (1979).

"The Reaction of Nickel Tetracarbonyl with γ-Alumina," R. B. Bjorklund and R. L. Burwell, Jr., J. Coll. Interface Sci., 70, 383 (1979).

"Adsorptive and Catalytic Properties of Isolated Units of $Fe_4S_4(SR)_4^{2-}$," R. G. Bowman and R. L. Burwell, Jr., J. Am. Chem. Soc., 101, 2877 (1979).

"Structure Sensitivity and Supported Platinum Catalysts," R. L. Burwell, Jr., 12th Jerusalem Symposium, B. Pullman, ed., 207 (1979).

"Effect of Steric Strains upon the Hydrogenation of Olefins and Acetylenes on Pd/SiO_2 and Pt/SiO_2," H. H. Kung and R. L. Burwell, Jr., J. Catal., in press.

"The Reaction between Hydrogen and Carbon Monoxide on Catalysts Derived from $Mo(CO)_6/Al_2O_3$," R. G. Bowman and R. L. Burwell, Jr., J. Catal., in press.

"An Infrared Study of the Physisorption and Reaction of Molybdenum Hexacarbonyl on γ-Alumina," M. Laniecki and R. L. Burwell, Jr., J. Coll. Interface Sci., in press.

"Pt/Al_2O_3 I. Percentage Exposed and Its Effect upon the Reactivity of Adsorbed Oxygen," M. Kobayashi, Y. Inoue, N. Takahashi, R. L. Burwell, Jr., J. B. Butt, and J. B. Cohen, J. Catal., in press.

"Pt/Al_2O_3 II. Activity and Selectivity Patterns for Methycyclopropane Hydrogenolysis and Cyclopentane Exchange with Deuterium: Comparison with Pt/SiO_2," S. S. Wong, P. H. Otero-Schipper, W. A. Wachter, Y. Inoue, M. Kobayashi, J. B. Butt, R. L. Burwell, Jr., and J. B. Cohen, J. Catal., in press.

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

2) Lectures and Presentations

R. L. Burwell

1) "Structure Sensitivity and Supported Platinum Catalysts", 12th Jerusalem Symposium "Catalysis and Biochemistry, Theory and Experiment," April 2-4, 1979, Jerusalem.

2) "Supported F-Element Organometallic Complexes: Surface Chemistry and Catalysis" Houston Meeting of American Chemical Society, March 24, 1980 (with T. J. Marks, R. G. Bowman, R. WaKamura and P. J. Fagan).

J. B. Butt

"Supported Metal Catalysts"

1) University of Ghent, Belgium, Jan. 1980

2) Louvaen - La Neuve University, Belgium, Jan. 1980

3) AICHE Annual Meeting, Miami Beach Fl. Nov. 1979

4) University of Delaware, Newark Del. March 1980

J. B. Cohen

1) "X-ray Studies of Catalysts", Universal Oil Products, Inc., Des Plaines, IL. Oct. 30, 1979.

Captions for Figures

Figure 1. Turnover frequency vs. percentage exposed for i-butane formation in MCP hydrogenolysis for standard pretreatment.

Figure 2. Selectivity (i-butane/n-butane) vs. percentage exposed for standard pretreatment.

Figure 3. Turnover frequency vs. percentage exposed for i-butane, comparison between cool in He and H_2.

Figure 4. Summary of structure sensitivity for i-butane formation.

Figure 5. Summary of structure sensitivity for selectivity ratio.

Figure 6. Particle-size distribution from in-situ x-ray diffraction, 6.3-SiO_2-PtCl-L. Treatment a: O_2 300°C, 0.5 h ; H_2, 300°C 1 h ; to 450°C and cool to R. T., in He.
b: O_2, 300°C, 0.5 h ; H_2, 25°C, 1 h.
c: O_2, 300°C, 0.5 h ; H_2, 200°C, 1 h ; cool to R. T. in H_2.
d: O_2, 300°C, 0.5 h ; H_2, 450°C, 1 h ; cool to 25°C in H_2.

Figure 7. Particle-size distribution from in-situ x-ray diffraction, 40-SiO_2-PtCl-S.

N_T VS. PERCENTAGE EXPOSED AT STANDARD PRETREATMENT CONDITION

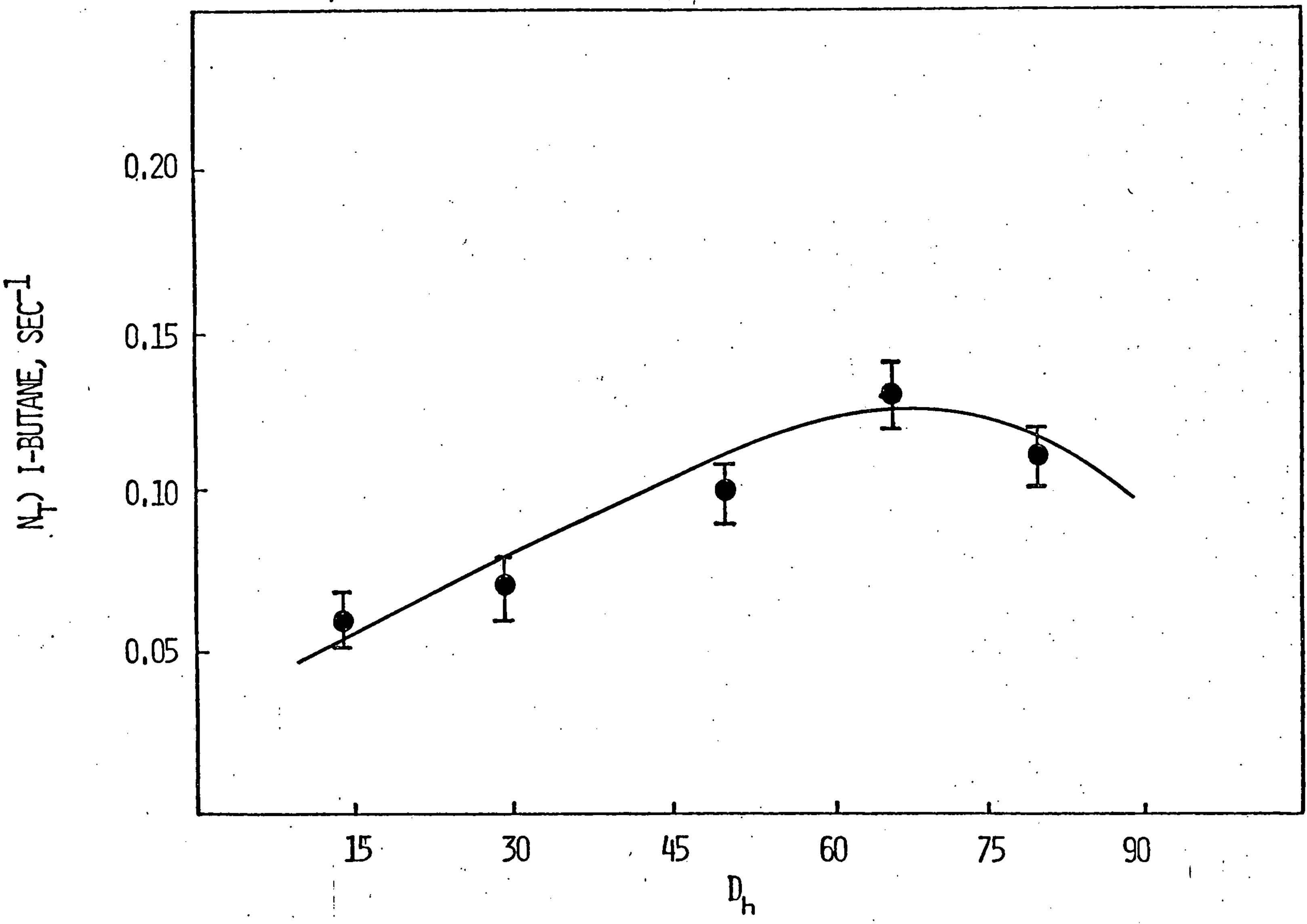


Figure 1

SELECTIVITY VS. PERCENTAGE EXPOSED AT STANDARD PRETREATMENT CONDITION

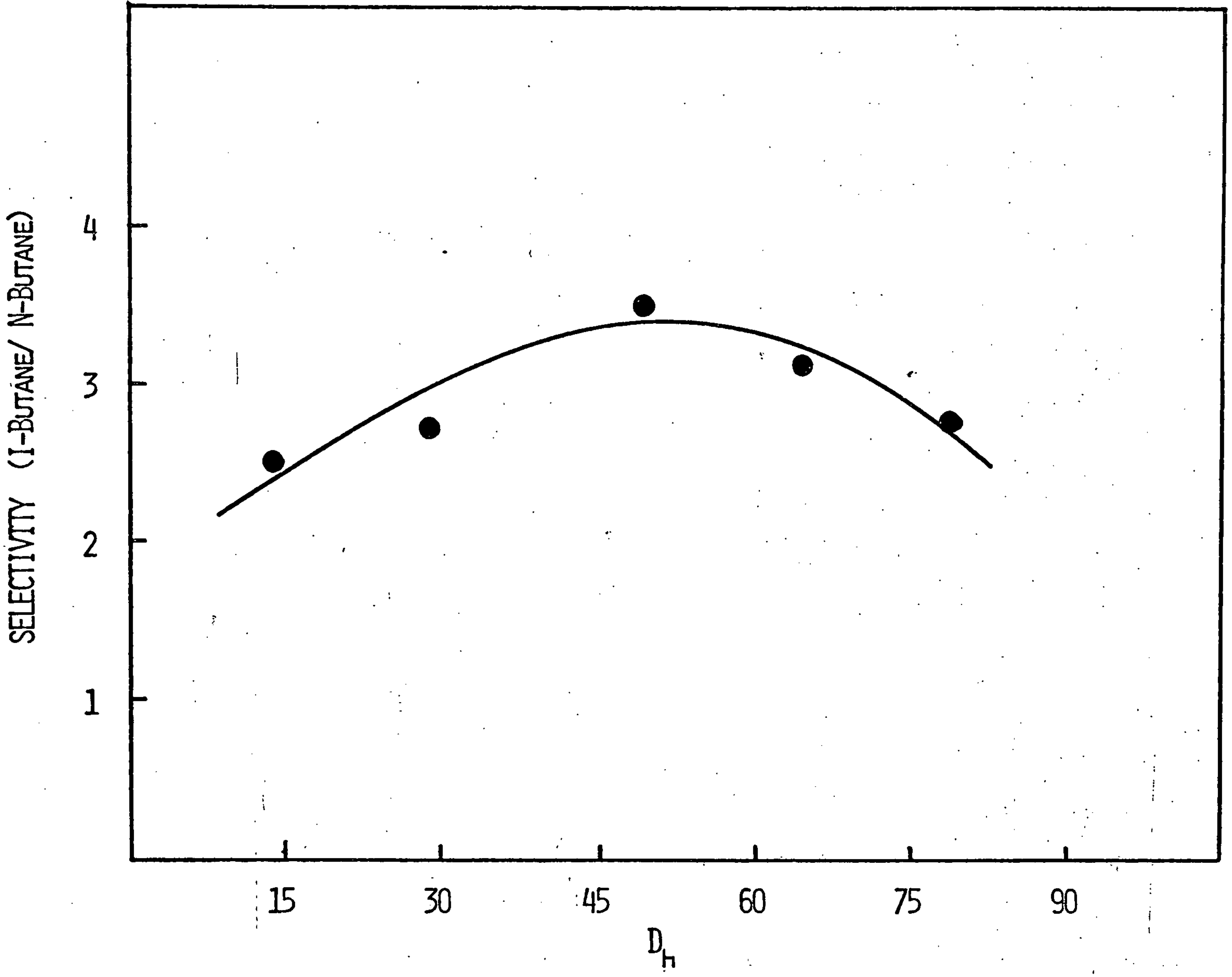
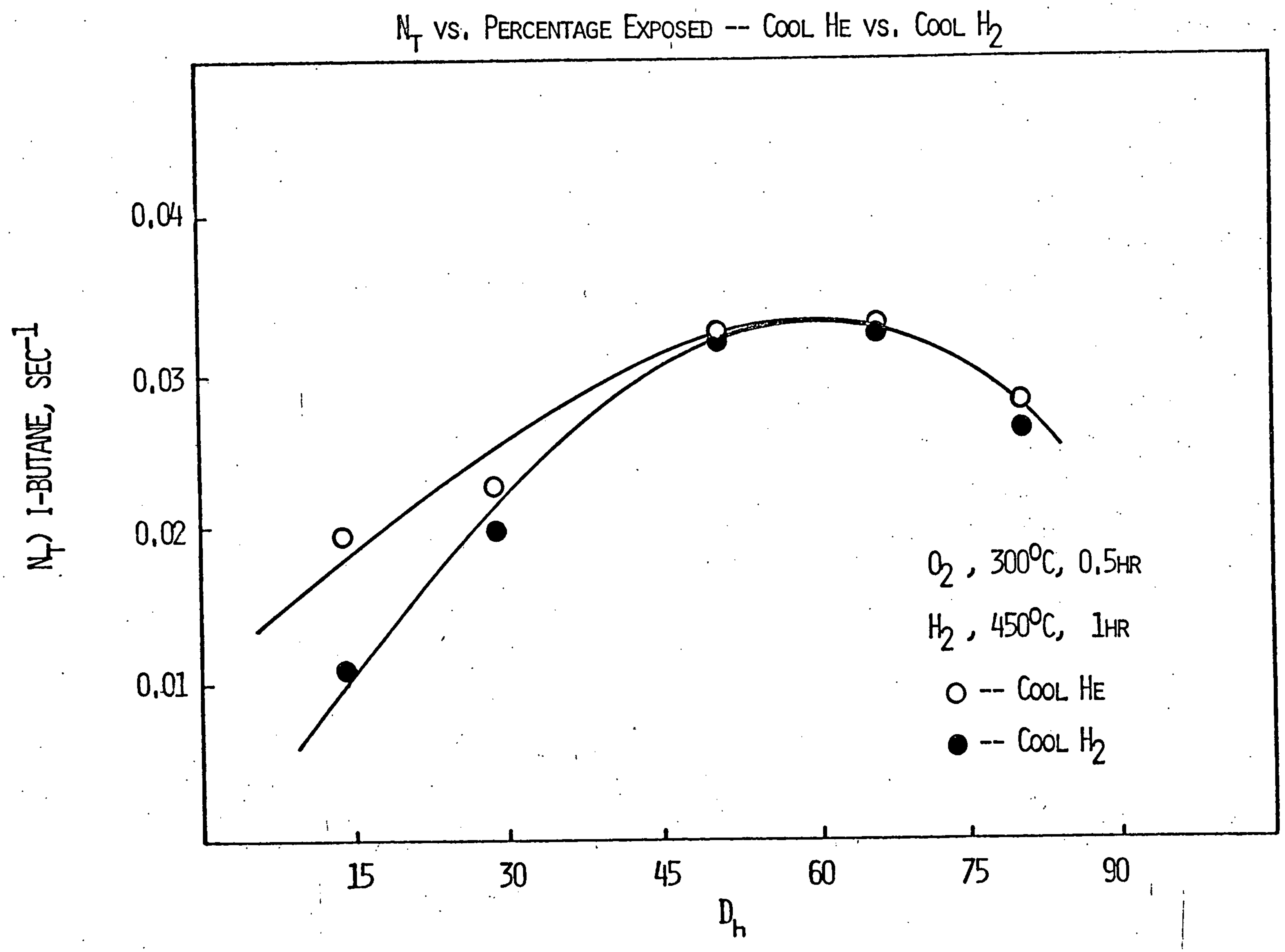


Figure 2



N_T VS. PERCENTAGE EXPOSED -- COOL HE VS. COOL H_2
N_T) I-BUTANE, SEC^{-1}
0.04
0.03
0.02
0.01
15
30
45
60
75
90
D_h
O_2 , 300°C, 0.5HR
H_2 , 450°C, 1HR
○ -- COOL HE
● -- COOL H_2

Figure 3

SUMMARY : STRUCTURE SENSITIVITY, Pd/SiO$_2$, I-BUTANE

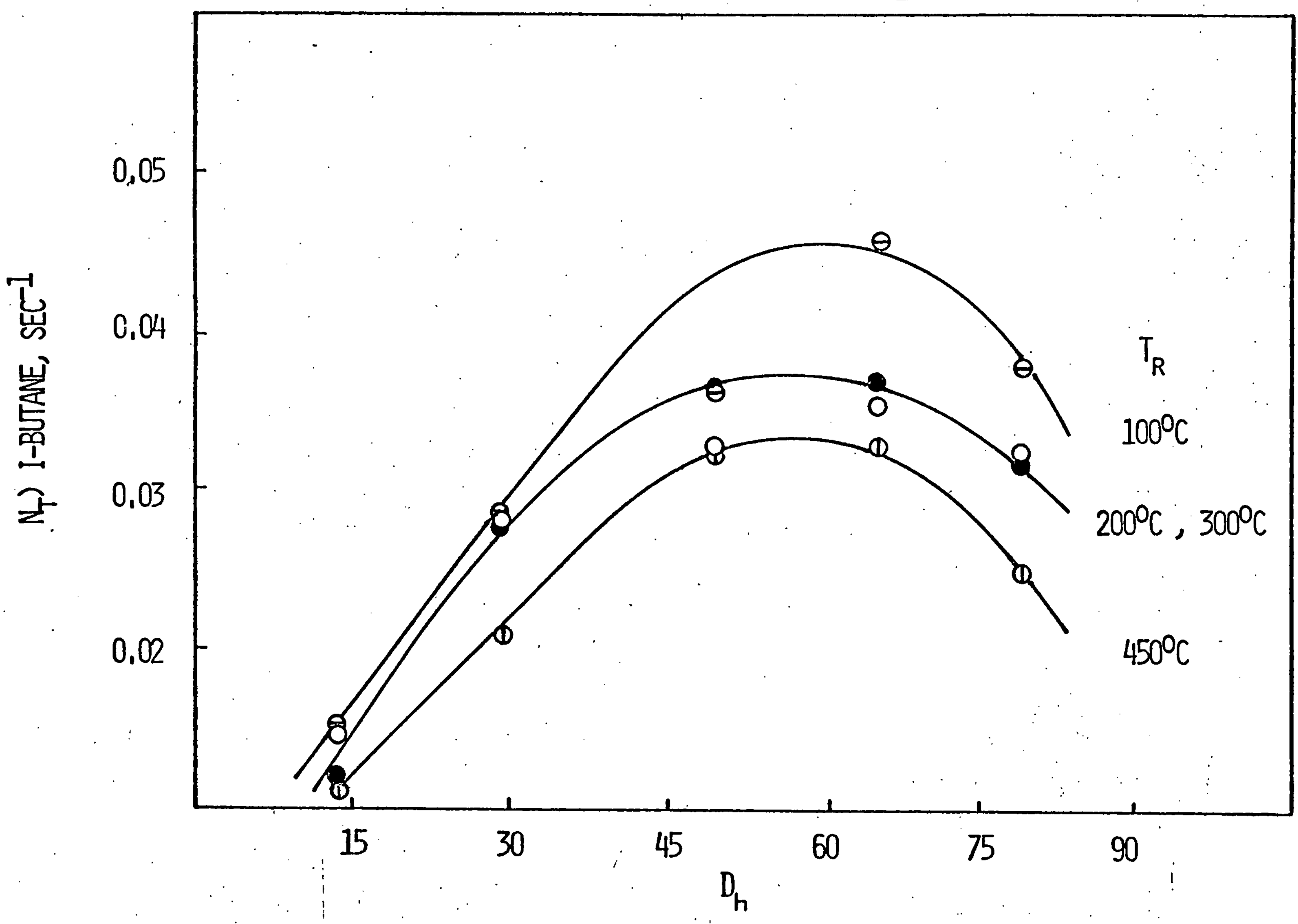


Figure 4

SUMMARY : STRUCTURE SENSITIVITY, Pd/SiO$_2$, SELECTIVITY

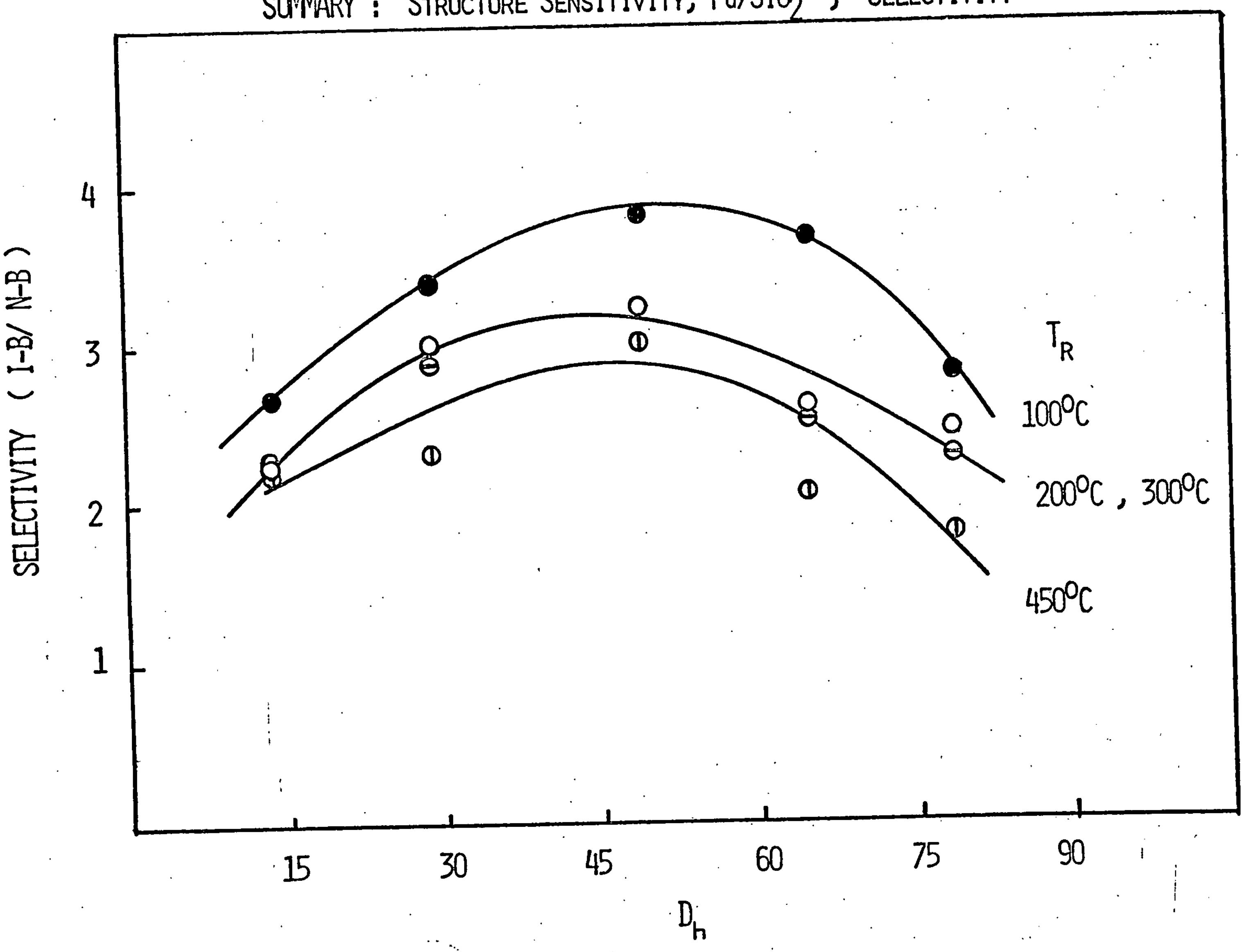


Figure 5

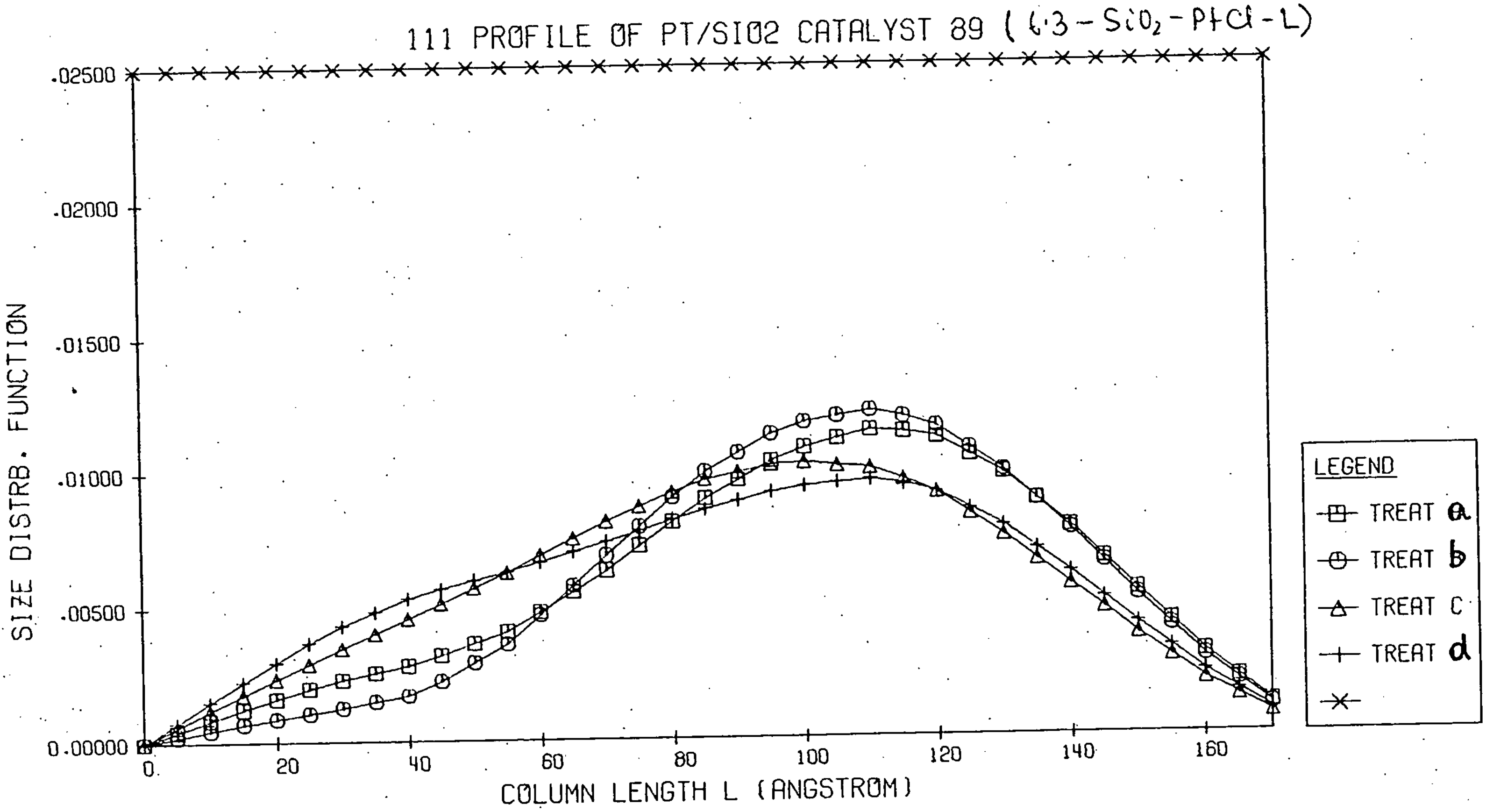
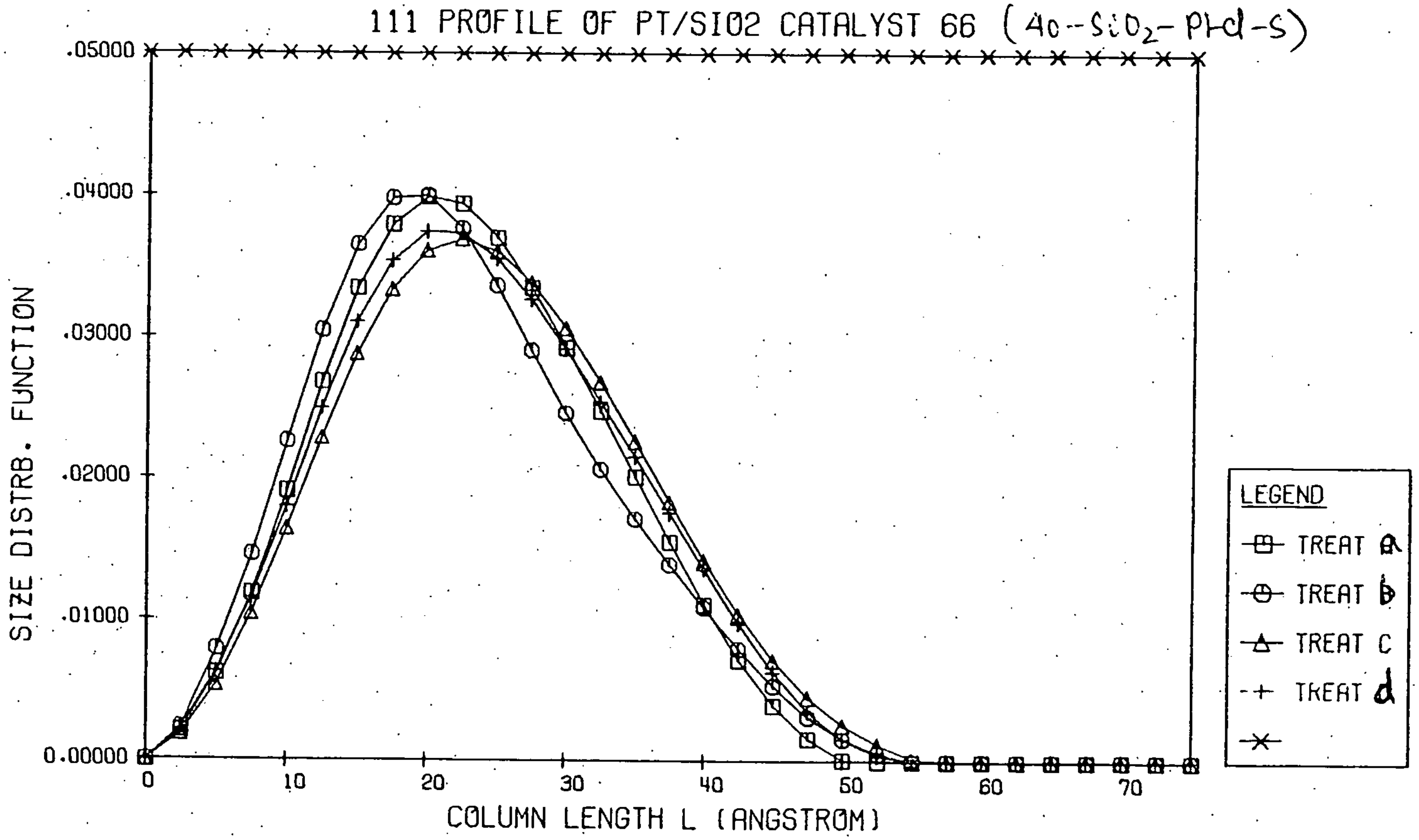

111 PROFILE OF PT/SIO2 CATALYST 89 (6·3-SiO2-PtCl-L)
SIZE DISTRB. FUNCTION
.02500
.02000
.01500
.01000
.00500
0.00000
0.
20
40
60
80
100
120
140
160
COLUMN LENGTH L (ANGSTROM)
LEGEND
TREAT a
TREAT b
TREAT C
TREAT d

Figure 6


111 PROFILE OF PT/SIO2 CATALYST 66 (40--SiO2-Pt-d-S)
SIZE DISTRB. FUNCTION
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.03000
.02000
.01000
0.00000
0
10
20
30
40
50
60
70
COLUMN LENGTH L (ANGSTROM)
LEGEND
TREAT a
TREAT b
TREAT C
TREAT d

Figure 7