Item 1

Report COO-4254-2

MASTER

Progress Report

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"The Properties of Supported Metal Catalysts"

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Abstract

The preparation and characterization of supported platinum catalysts has been extended to a series of alumina— supported catalysts similar to the previously investigated platinum - silica series. Characterization has been carried out via hydrogen chemisorption, hydrogen-oxygen titration, hydrogenolysis of methylcyclopropane and deuterium exchange with cyclopentane. In all, some twenty catalysts, with platinum percentage exposed ranging from 4.1 to 103% have been prepared and characterized. As was the case for the silica supported platinum, the specific conditions of catalyst pretreatment have been found to affect substantially the structure sensitive behavior in all cases. In addition, the thermal conditions employed in catalyst preparation affect the nature of structure sensitive behavior, which was not the case for Pt/SiO_2.

Substantial effort has been devoted to the development of a suitable system for making X-ray measurements in controlled atmospheres. Several of the Pt/SiO_2 catalysts have been investigated in hydrogen atmospheres, with the curious result that the apparent loading of metal detected in hydrogen is lower than that determined in air (which agreed with the value determined in preparation). This phenomenon is being investigated further. Finally, we have begun to examine the Pt/Al_2O_3 series; current efforts are aimed at finding loading levels which provide adequate intensity.

Preparation of the Pt/Al_2O_3 Series

During the term of this contract we have concluded the work on structure sensitivity of methylcyclopropane hydrogenolysis and deuterium-cyclopentane exchange on Pt/Al_2O_3. In the last progress report (COO-4254-1) we described some difficulties in preparing a set of Pt/Al_2O_3 catalysts with examples in the low range of percentages exposed (D_h). In part, this problem arose because of our requirement that no treatment during catalyst preparation should exceed about 450°C. This requirement insured that the alumina surface of various catalysts would all be in the same state after our standard pretreatment in the apparatus, O_2, 300°; H_2, 300°; Ar or He, 450°. We specifically wished to avoid preparing catalysts of low D_h by sintering at 700°C or thereabouts as has sometimes been done in the past.

Research disclosed that a key item in determining the value of D_h was the amount of water bound to the catalyst at the start of reduction. Dry catalysts gave large values of D_h, 90-100%, upon reduction whereas wet catalysts led to values of D_h of about 4%. The particles here are about 250 Å in diameter and, thus, larger than the pore structure of the alumina. Intermediate water contents give intermediate values of D_h.

Using this information some 50-100 g batches of Pt/Al_2O_3 were prepared from alumina (American Cyanamid Aero Extudate - 1000, 60-80 mesh) impregnated with $Pt(NH_3)_2(NO_2)_2$ aq. In addition, preparation of catalysts by impregnation with $Pt(NH_3)_4(NO_3)_2$ aq was investigated. This preparation gave results almost identical with that using $Pt(NH_3)_2(NO_2)_2$. A list of catalysts prepared is given in Table 1.

The nomenclature for the catalysts is as follows: the first term is the percentage exposed of the catalyst determined by hydrogen chemisorption

Table 1

Summary of Preparation Procedures of Catalysts

Catalyst	Wt. % Pt	Calcination Temp, °C/Time, h.		Reduction Temp, °C/Time, h.	
3.1-Al_2O_3-PtNN-L	0.80	----		300	2
4.1-Al_2O_3-PtNN-H	0.300	400	4	500	18
4.2-Al_2O_3-PtNN-L	0.212	85	ON	300	2
9.0-Al_2O_3-PtNN-L	0.230	----		300	2
22 -Al_2O_3-PtNN-L	0.230	100	2	300	2
27 -Al_2O_3-PtN -H+*	0.310	500	3	500	2.5
32 -Al_2O_3-PtCl-H	0.234	500	1	500	2.5
36.1-Al_2O_3-PtNN-L	0.289	85	ON	300	2
40 -Al_2O_3-PtNN-L	0.212	91	18	300	2
40.7-Al_2O_3-PtN -H+*	0.288	500	2	500	1
43.6-Al_2O_3-PtNN-H*	0.330	400	1.5	500	225
47.6-Al_2O_3-PtNN-H*	0.307	400	1	500	26
53 -Al_2O_3-PtNN-L	0.230	80	1.75	300	2
66.7-Al_2O_3-PtNN-L	0.274	220	3	300	2
72.4-Al_2O_3-PtNN-L	0.282	85	ON	200	2.5
73.2-Al_2O_3-PtN -L+*	0.323	270	3	300	1
74 -Al_2O_3-PtNN-H*	0.297	400	1	500	10
88 -Al_2O_3-PtNN-L	0.230	200	2	300	2
88.4-Al_2O_3-PtNN-H	0.293	400	1	500	49
94.2-Al_2O_3-PtNN-H	0.301	400	4	400	2.8
95.5-Al_2O_3-PtNN-H	0.295	400	2.5	400	3
96.7-Al_2O_3-PtNN-L	0.293	400	1	300	2
100.9-Al_2O_3-PtNN-L	0.293	400	1	300	25
103.8-Al_2O_3-PtNN-H	0.293	400	1	500	2
103.8-Al_2O_3-PtNN-L	0.230	----		300	2
107 -Al_2O_3-PtNN-L	0.212	200	0.33	300	2
136 -Al_2O_3-PtNN-L	0.238	----		300	2

ON = Over Night

\+ Catalysts were calcined in muffle furnace; all others were calcined in flowing oxygen.

* Impregnation using evaporation to dryness over water bath; all others were impregnated using incipient wetness technique.

the third term represents the preparation compound used (PtCl indicates H_2PtCl_6, PtN for $Pt(NH_3)_2(NO_2)_2$ and PtNN for $\{Pt(NH_3)_3(NO_2)\}.(NO_2)\}$; The last term indicates whether the catalyst underwent low or high temperature calcination and reduction after impregnation. L represents calcination and reduction at or below 300°C whereas H is for calcination and reduction at 400°C or above. For example, 36-Al_2O_3-PtNN-L indicates a catalyst impregnated by $\{Pt(NH_3)_3(NO_2)\}(NO_2)$ solution, calcined and reduced at or below 300°C.

Characterization by Chemisorption and BET Area

We determined values of D_h and D_t on a series of Pt/Al_2O_3 catalysts as we had earlier done with Pt/SiO_2. D_h is the percentage exposed from hydrogen chemisorption assuming that $H/Pt_s = 1$. D_t is determined by the measurement of the hydrogen uptake of platinum which was initially clean and was then treated for 15 min with oxygen at 25°C. In essence, it assumes that $O/Pt_s = 1$. Between $D_h = 4$ and 40%, D_h and D_t are nearly identical. At larger D_h, the ratio becomes progressively greater than unity. We obtained catalysts with measured values of D_h like 107 and 130%. Of course, these values cannot be correct and such materials probably involve ratios of H/Pt_s which exceed unity. On Pt/SiO_2, there was good evidence that O/Pt_s was less than unity at an exposure of 15 min but we found no catalysts in which D_h exceeded 100%.

A few experiments were run on Pt/SiO_2 catalysts. There have been several reports in the literature that platinum could strongly adsorb nitrogen at lower temperatures. We investigated this matter for Pt/SiO_2, D_h = 63.5%. We could find no adsorption of nitrogen which was irreversible at

-78° or 25°C. We also rechecked an earlier conclusion that Pt/SiO_2 catalysts cooled in hydrogen from 450°C contained hydrogen in excess of that after chemisorption of hydrogen on catalyst cooled from 450°C in argon. A technique improved over that used previously was employed. We established that the amount of hydrogen adsorbed on clean Pt in 1 h at 25°C was the same as that adsorbed from 5 pulses (about 30 sec) and that the catalyst cooled from 450 or 500°C contained about 25% more hydrogen.

The BET surface area was determined for the calcined and reduced support alone (125 m^2/g) and for 4.1, 32, 40.7 and 94 percent exposed samples. Only 4.1-Al_2O_3-PtNN-H had a surface area lower than the blank (104 m^2/g); this may represent some pore blocking since the average dimension of the metal particles here is approximately the same as the pore diameter (∿18 nm).

Characterization by Chemical Reactivity

The structure sensitivity of the hydrogenolysis of methylcyclopropane (MCP) is dependent upon the temperature of pretreatment of the catalyst in flowing hydrogen prior to carrying out the reaction at 0°C, 16:1::H_2:MCP. This dependence is quite similar to that reported for the same reaction on Pt/SiO_2. In addition, we detect a difference in the level of activity (although no difference in the general nature of structure sensitivity) dependent upon the thermal conditions employed in the initial catalyst preparation. Those catalysts reduced at high temperature in preparation (400° - 500° designated H in Table 1) were on average about 50% higher in activity than those reduced at low temperature (300°, designated L). This effect, and the variation in structure sensitivity with prereduction temperature, is shown in Figures 1 and 2 for the turnover frequency of formation of the major i-butane product, and the summary of a large number of experiments is given in Figure 3. Note that the high temperature preparation low temperature pretreat catalysts are essentially equivalent in activity to the low temperature preparation high temperature pretreat materials, and the effect of preparation conditions disappears completely for very low temperature pretreats (25°C). The selectivity is also independent of preparation conditions, as shown in Figure 4 for catalysts pretreated at 370°C.

As was the case for Pt/SiO_2, the activation energies of the hydrogenolysis reactions are independent of the percentage exposed and of all pretreatment and preparation thermal history. These values averaged 36.4 ± 2.3 KJ/mole for i-butane formation and 43.4 ± 3.6 KJ/mole for n-butane formation (about the same as for Pt/SiO_2). The resultant selectivities decrease monotonically from about 15 ($i\text{-}C_4/n\text{-}C_4$) to 9 as temperature of reaction is increased from 0 to 35°C. Selectivity is structure insensitive at all temperatures investigated in this range.

Some comparison with results previously obtained with Pt/SiO_2 for MCP hydrogenolysis is given for turnover frequency in Figure 5 and selectivity in Figure 6. The comparison is made for pretreatment temperature of 480°C, corresponding to the conditions employed in the Pt/SiO_2 studies. There is no strong effect of the support on the turnover frequency or selectivity, indicative of similar metal-support interactions for the two series of catalysts. This is somewhat surprising in view of the commonly voiced idea that metal-support interactions are much stronger for alumina than for silica. However, most Pt/Al_2O_3 catalysts contain significant amounts of chloride retained after impregnation with $HPtCl_6$, and this is known to affect the catalytic properties of the metal. As shown in Table 1, with a single exception (and it is not included in the comparison here) none of our Pt/Al_2O_3 catalysts contained chloride.

The details of structure sensitivity do differ between the two supports at identical pretreatment conditions, since the reaction is structure insensitive on Pt/Al_2O_3 and varies by a factor of about 4 with increasing D_h on Pt/SiO_2.

The investigation of the effect of D_h upon the isotopic distribution patterns of cyclopentane exchanged with deuterium on Pt/Al_2O_3 catalysts at about 81°C has also been completed. The following pretreatment conditions were investigated: standard, O_2, 300°; H_2, 100°, and O_2, 300°; H_2, 450°. The effect of conditions of pretreatment upon rates was similar to that observed in the hydrogenolysis of methylcyclopropane. Definite but overall not very large variations of the distribution pattern were observed as illustrated in Figure 7. Pt/SiO_2 and Pt/Al_2O_3 catalysts give the same general type of isotopic distribtuion pattern but there are some definite differences particularly at large values of D_h.

During isotopic exchange, the rate declined slowly. It is likely that the deactivation resulted from deposition of carbonaceous residue on the catalyst. This was investigated on several Pt/Al_2O_3 catalyst by interupting an exchange experiment at 81°C with a purge of helium. This was followed by exposure to flowing hydrogen and trapping evolved hydrocarbons. The amount and identity of hydrocarbon released at 100, 200, 300, and 450°C was found. Unlike silica gel the support alone retains cyclopentane. Most is released at 100°C. Almost all hydrocarbon released from Pt/Al_2O_3 was cyclopentane and most was released by 200°C. This was also true for Pt/SiO_2. Thus, the carbonaceous residue still maintains the C_5-ring structure.

A substantial amount of work has been done in preliminary work aimed at at the preparation of a set of Pd/SiO_2 catalysts with a wide range of percentage exposed. Previous literature did not disclose how to prepare such a set of catalysts without recourse to sintering at high temperatures. It is easy to prepare Pd/SiO_2 of large values of D_h. Silica gel ion-exchanged with $Pt(NH_3)_4^{2+}$ and calcined at 435°C gives catalysts with D_h of about 20%. However, the Pd analog gives catalysts of large D_h. If the silica gel ion exchanged with $Pd(NH_3)_4^{2+}$ was reduced in wet hydrogen, we obtained values of D_h in the vicinity of 40%. A number of attempts to prepare catalysts with D_h in the vicinity of 10-20% failed. However, silica gel impregnated with palladium acetylacetonate and reduced directly gave D_h near 10% and calcined at 300°C and then reduced gave D_h near 30%. We believe that we now know how to prepare the desired range of D_h for Pd/SiO_2 catalysts.

Related Work - Chemical Reactivity Characterization

In work related to but not supported by this project, the isotopic exchange between 2, 2-dimethylbutane (neohexane) and deuterium was investigated on the platinum/silica catalysts. It was of interest to discover whether particle size affected the relative degree of exchange of the CH_2 hydrogen atoms which should by hindered by the adjacent t-butyl group. One might expect the exchange to occur more readily at edge than at face atoms of platinum. Such an effect was found although it is smaller than we had expected.

The role of carbonaceous deposits in reactions of hydrocarbons on noble metal catalysts has been of considerable interest recently. We have investigated this using our Pt/SiO_2 catalysts but not with DOE support. At -78 to 25°C, the hydrogenation of ethylene and the hydrogenolysis of cyclopropane appear to proceed on the actual surface of the metal and not on sites in a carbonaceous overlayer.

Dr. N.W. Cant of Macquarie University in Australia is investigating the effect of D_h in our set of Pt/SiO_2 catalysts on the oxidation of carbon monoxide by oxygen. These experiments employ a few percent each of oxygen and carbon monoxide in flowing helium carrier. At 180°C, the turnover frequency is between 0.01 and 0.015 without trend in D_h.

Characterization by X-ray Diffraction Methods

A large effort was expended to develop a suitable system for making measurements in various gas environments, H_2, He or O_2. The gas manifold is shown in Figure 8 with the sample cell on the far left. (The catalyst is in the vertical tube in the small furnace; by tilting it can be moved to the disc-like region of the cell.) The cell is shown in Figure 9, and on a diffractometer in Figure 10. This cell is covered with a thin mica sheet, epoxied to the glass. X-ray absorption is not too bothersome if the mica is sufficiently thin, and a small tilt of the cell minimizes mica reflections. Other more permanent windows, such as Be, gave reflections that interfered with those from the catalyst. The cell can be tested for leakage by reducing MnO in situ and leaving the cell for several days. Leakage of oxygen will change the color from light green to brown. An added feature of this cell is that it is transportable; it can be used to carry pretreated specimens to future studies at a synchrotron. Several such cells have been constructed and can be employed on almost any diffractometer.

In addition to constructing and testing this cell, we have made tests of the method we proposed for Fourier analysis of X-ray peak shape with a single peak, rather than the two or more peaks usually involved. We had hoped that we could employ a completely on-line mini-computer system for this purpose. Indeed, we have tested such a system, but the weak signals from the dilute catalysts we are using in this study require that the data be taken and smoothed before Fourier-inverting; on-line determinations are erratic. Nonetheless, we expect this method to be a considerable time saver in the future, and especially in our studies of Pt/Al_2O_3, where there is only one metal peak free of interference from the support.

Studies with the new cell are well underway. Pt/SiO_2 catalysts with 66, 36 and 7 percent exposed have been examined after exposure to oxygen (at 300°C, 1/2 hr.) and then reduced in H_2 at various temperatures from 25°C to 450°C. Such studies were undertaken to explore in more detail the observed dependence of structure sensitivity on pretreatment conditions noted for both exchange and hydrogenolysis reactions, and the difference in the reactivity of chemisorbed oxygen after short or long term exposure to this gas. As we have found a good correlation between Pt atom vibrations (measured in air) and turnover number; perhaps it is changes in these vibrations that are causing such effects. Attempts to determine the mean-square vibrational amplitudes of Pt/SiO_2 in these various atmospheres were not successful because the intensities of several of the peaks were too weak due to the mica windows. This work will be repeated with our more intense rotating anode X-ray generator.

In the course of this work, however, a curious effect has been detected. When the catalyst is examined in air, the volume fraction of Pt agrees with the loading determined in preparation, but when the catalyst is exposed to H_2 at modest temperatures, the percent loading of Pt in the catalyst appears to drop considerably. It is as if we are seeing only the larger sizes. Perhaps the H_2 is modifying the surface of the particles so that the smaller ones, which have a larger percentage of near-surface atoms, "disappear". It is common thought that only oxygen does this damage, but the X-ray determined Pt loading for samples stored in air is not low, as mentioned earlier. We have seen this effect in two catalysts, but we will check it one more time.

So far there has been very little high-flux time at the Stanford synchrotron, so that we have been unable to examine the Pt/SiO_2 with 63 and 81 exposed. With these catalysts, the Pt peaks are so broad and weak that they cannot even by found with a rotating anode unit. We wish to determine whether Pt is still fcc at these sizes and if PtO forms. Indeed, are these particles crystalline Pt? The staff at the Cornell synchrotron has agreed to allow us to install a diffractometer at their storage ring, which will be operational this spring, and we hope to have more beam time there anyway. Accordingly, we are modifying a diffractometer for this purpose.

We had proposed to develop an EXAFS systems for examining the most dispersed catalysts, in air and various other gaseous environments. Suitable high-speed counting electronics has been obtained, and a student is being trained by spending several months with the EXAFS group at Argonne National Laboratory. These developments involve funds from other sources, as the instrument is of interest to several projects here. It is expected that the system will be ready by next winter.

Finally, we have begun to examine Pt/Al_2O_3 catalysts. Present experiments are directed at establishing the loading required for adequate intensity. Pt/Al_2O_3 with 0.8 wt percent Pt was not appropriate and we are now examining one with 2.7 percent Pt. If this is successful the reactivity will be studied to correlate with changes in peak shape.

Work Projected Between 1 March and 30 June, 1979

Chemical Reactivity Characterization

1) We plan to prepare 100 g quantities of Pd/SiO_2 of a wide range of D_h. We plan to prepare the catalysts by ion exchange between silica gel and $Pd(NH_3)_4(NO_3)_2$ rather than $Pd(NH_3)_4Cl_2$ to avoid the presence of chloride ion. We will then start the investigation of isotopic exchange between cyclopentane and deuterium and methylcylopropane hydrogenation on these catalysts.
2) We also plan to run certain experiments aimed at clarifying the interaction of oxygen and hydrogen with Pt/Al_2O_3 as a function of D_h, in view of the values greater than 100 percent obtained for some of these catalysts.

X-ray Characterization

1) The synchrotron diffractometer will be completed and installed at Cornell, and preliminary measurements will be carried out.
2) Development of the EXAFS system will be pursued.
3) Data for volume fraction and Fourier analysis of peak shape of three Pt/SiO_2 catalysts in various gas environments will be taken and analyzed, and compared to reactivities.

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% of his time on this project. Summer effort was 100% of time for one month for R.L. Burwell and J.B. Cohen. The 8% time effort will be continued until 30 June, 1979. A full time graduate research assistant, Mr. Steven Wong, has been associated with this project during the entire term of the present contract (J.B. Butt); Dr. M. Kobayashi was a postdoctoral fellow from 5/1/78 - 8/31/78 and Dr. N. Takahashi from 9/1/78 to date (R.L. Burwell); Dr. F. Molinaro was a postdoctoral fellow from 4/1/78 - 7/31/78 and Dr. R. Nandi from 10/1/78 to date (J.B. Cohen).

Publications and Other Activities

1) Publications

T. Uchijima, J.M. Herrmann, Y. Inoue, R.L. Burwell, Jr., J.B. Butt, and J.B. Cohen, "Pt/SiO_2, Part I. Percentage Exposed and Its Effect Upon the Reactivity of Adsorbed Oxygen", J. Catalysis, 50, 464-478 (1977).

S. Sashital, J.B. Cohen, J.B. Butt, and R.L. Burwell, Jr., "Pt/SiO_2, Part II. Characterization of the Gel and the Platinum Particles by X-ray Diffraction", J. Catalysis, 50, 479-493 (1977).

P.H. Schipper, W.A. Wachter, J.B. Butt, R.L. Burwell, Jr. and J.B. Cohen, "Pt/SiO_2, Part III. Activity and Selectivity for Some Hydrogenation Reactions", J. Catalysis, 50, 494-507 (1977).

Y. Inoue, J.M. Herrmann, H. Schmidt, R.L. Burwell, Jr., J.B. Butt and J.B. Cohen, "Pt/SiO_2, Part IV. Isotopic Exchange Between Cyclopentane and Deuterium", J. Catalysis, 53, 401-413 (1978).

P.H. Otero-Schipper, W.A. Wachter, J.B. Butt, R.L. Burwell, Jr. and J.B. Cohen, "Pt/SiO_2, Part V. The Effect of Pretreatment on Structure Sensitivity for Methylcyclopropane Hydrogenation Activity and Selectivity", J. Catalysis, 53, 414-422 (1978).

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

2) Lectures and Presentations

R.L. Burwell

a) Midwest Regional Meeting of the American Chemical Society, Fayetteville, Ark., 26 October, 1978. "Effect of Cluster Size and Pretreatment Conditions Upon the Catalytic Activity of Pt/SiO_2 and Pt/Al_2O_3 Catalysts".

b) Twelfth Jerusalem Symposium, International Symposium on Catalysis in Chemistry and Biochemistry, Jerusalem, 2-6 April, 1979, "The Physical Nature and the Catalytic Characteristics of Supported Metal Catalysts".

J.B. Butt

a) "Some Comparisons of the Reactivity of Pt/SiO_2 and Pt/Al_2O_3", Seminar at Ashland Chemical Research Laboratory, Colombus, Ohio, April, 1978.

b) "Effect of Conditioning on the Activity of Pt/SiO_2 and Pt/Al_2O_3", Seminar at Department of Engineering Sciences, University of California, La Jolla, CA, June, 1978.

c) "Some Structure Sensitive Properties of Supported Metal Catalysts", Seminar at Department of Chemical Engineering, Princeton University, Princeton, N.J., Octobert, 1978; also at Chevron Research Company, Richmond, California, October, 1978.

d) "The Effect of Pretreatment Upon the Properties of Pt/SiO_2 and Pt/Al_2O_3", Paper presented at 71st Annual Meeting, American Institute of Chemical Engineers, Miami Beach, Florida, November 1978; also given at Celanese Research Company, Summit, N.J., January, 1979; also to be given as a Seminar at Lawrence-Berkeley Laboratory, April, 1979.

J.B. Cohen

a) "X-ray Studies of Pt/SiO_2 Catalysts", American Crystallographic Association, Winter Meeting, Karcher Symposium on Catalysis, University of Oklahoma, Norman, Oklahoma, March 21, 1978.

b) "Modern X-ray Studies of Catalyst Perfection", 85th Meeting of the American Institute of Chemical Engineers, Philadelphia, Penn., June 5, 1978.

Captions for Figures

Figure 1. Turnover Frequency vs. Percentage Exposed for i-Butane Formation in MCP Hydrogenolysis; Pretreatment in Hydrogen at 370°C, 1 hr.

Figure 2. Turnover Frequency vs. Percentage Exposed for i-Butane Formation in MCP Hydrogenolysis; Pretreatment in Hydrogen at 480°C, 1 hr.

Figure 3. Summary of Structure Sensitivity of i-butane Formation on Pt/Al_2O_3.

Figure 4. Selectivity (i-butane/n-butane), for MCP Hydrogenolysis on Pt/Al_2O_3.

Figure 5. Comparison of Turnover Frequencies on Pt/SiO_2 and Pt/Al_2O_3 for MCP Hydrogenolysis.

Figure 6. Comparison of Selectivity between Pt/SiO_2 and Pt/Al_2O_3.

Figure 7. Distribution Patterns for Deuterium Exchange with Cyclopentane on Pt/Al_2O_3.

Figure 8. 1-B, 2-B, 3-B: Nupro bellows valves for turning gas flow (H_2, He or O_2) on or off. 1-A, 2-A, 3-A: Whitley needle valves for flow rate. 3-C, 2-C, 1-C vent valves. The U-tubes are filled with silica gel to trap impurities and are normally surrounded by cold traps. The sample cell can be seen on the far left, tilted so that the catalyst is in a glass tube in the furnace. (After a gas treatment the cell is tilted so that the catalyst is in the disc-like chamber.)

Figure 9. The cell. C-2: Rotaflow valve to introduce the catalyst. C-1: Rotaflow valve that attaches to manifo ld in Figure 1. C-3: Kontes vacuum valve; gas outlet to flow meter.

Figure 10. Cell on diffractometer.

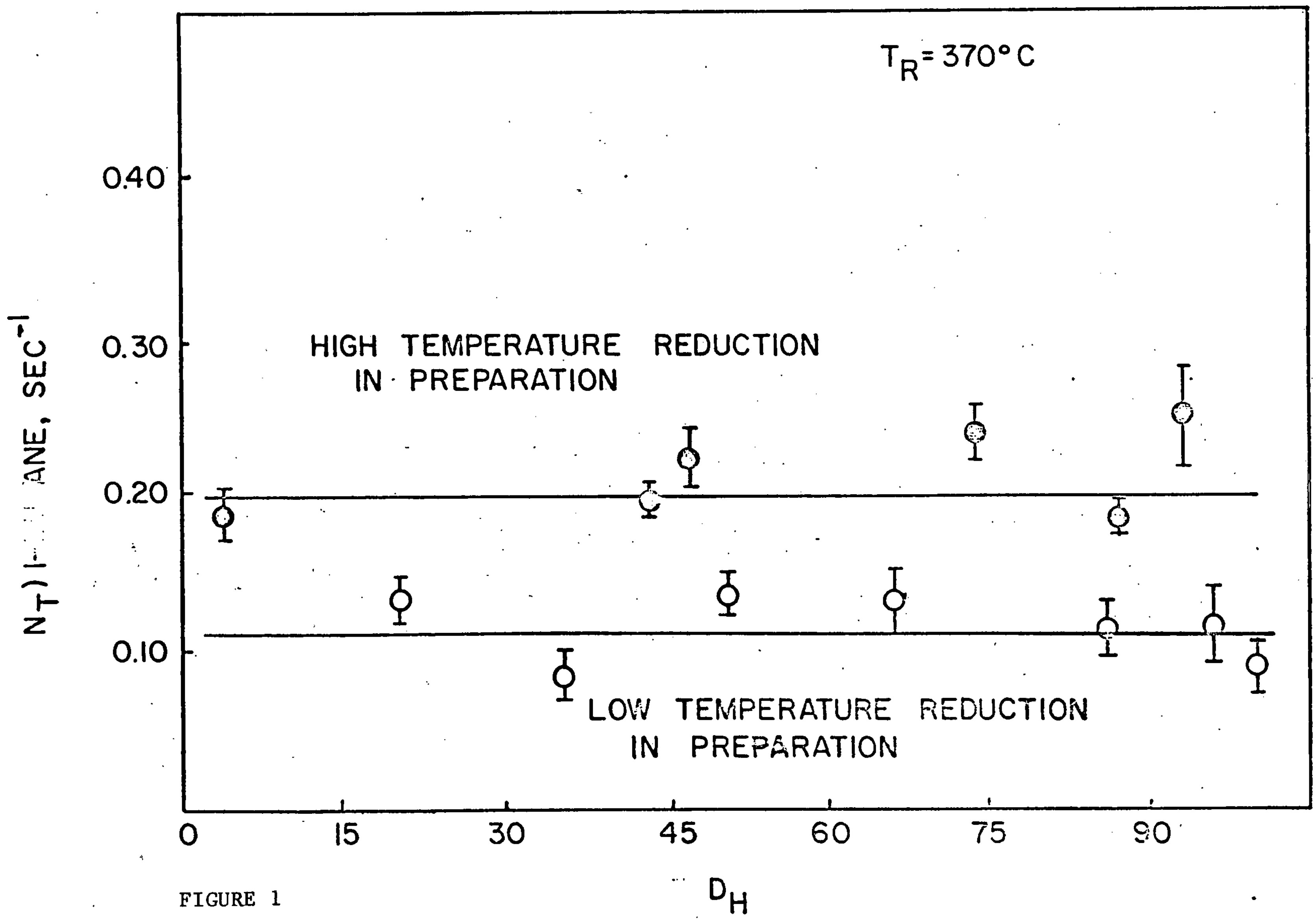
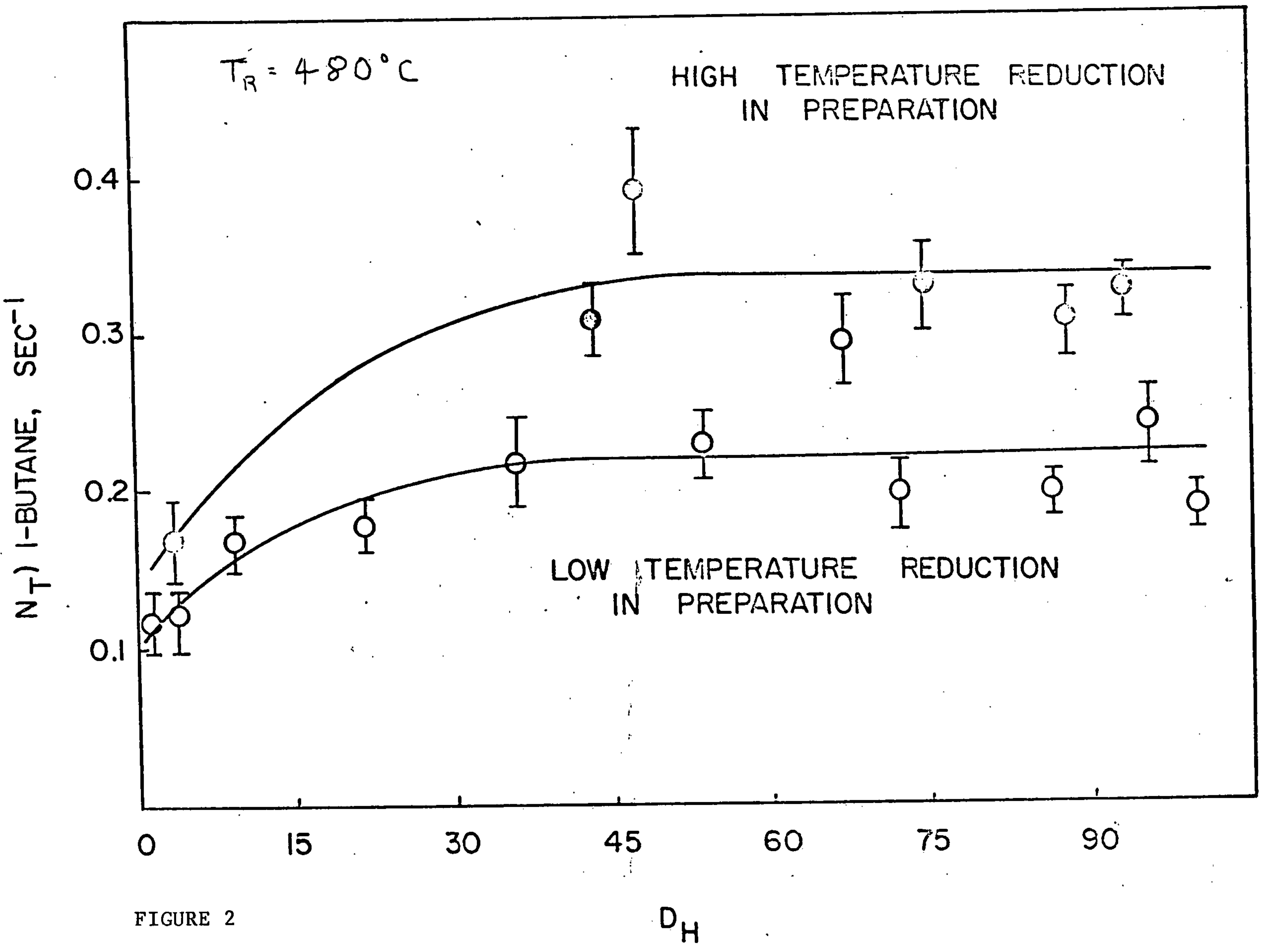

$T_R = 370°C$
0.40
0.30
0.20
0.10
HIGH TEMPERATURE REDUCTION IN PREPARATION
LOW TEMPERATURE REDUCTION IN PREPARATION
0
15
30
45
60
75
90
D_H
$N_T)$ ANE, SEC^{-1}

FIGURE 1



$T_R = 480°C$
HIGH TEMPERATURE REDUCTION IN PREPARATION
LOW TEMPERATURE REDUCTION IN PREPARATION
N_T) i-BUTANE, SEC^{-1}
0.4
0.3
0.2
0.1
0
15
30
45
60
75
90
D_H

FIGURE 2

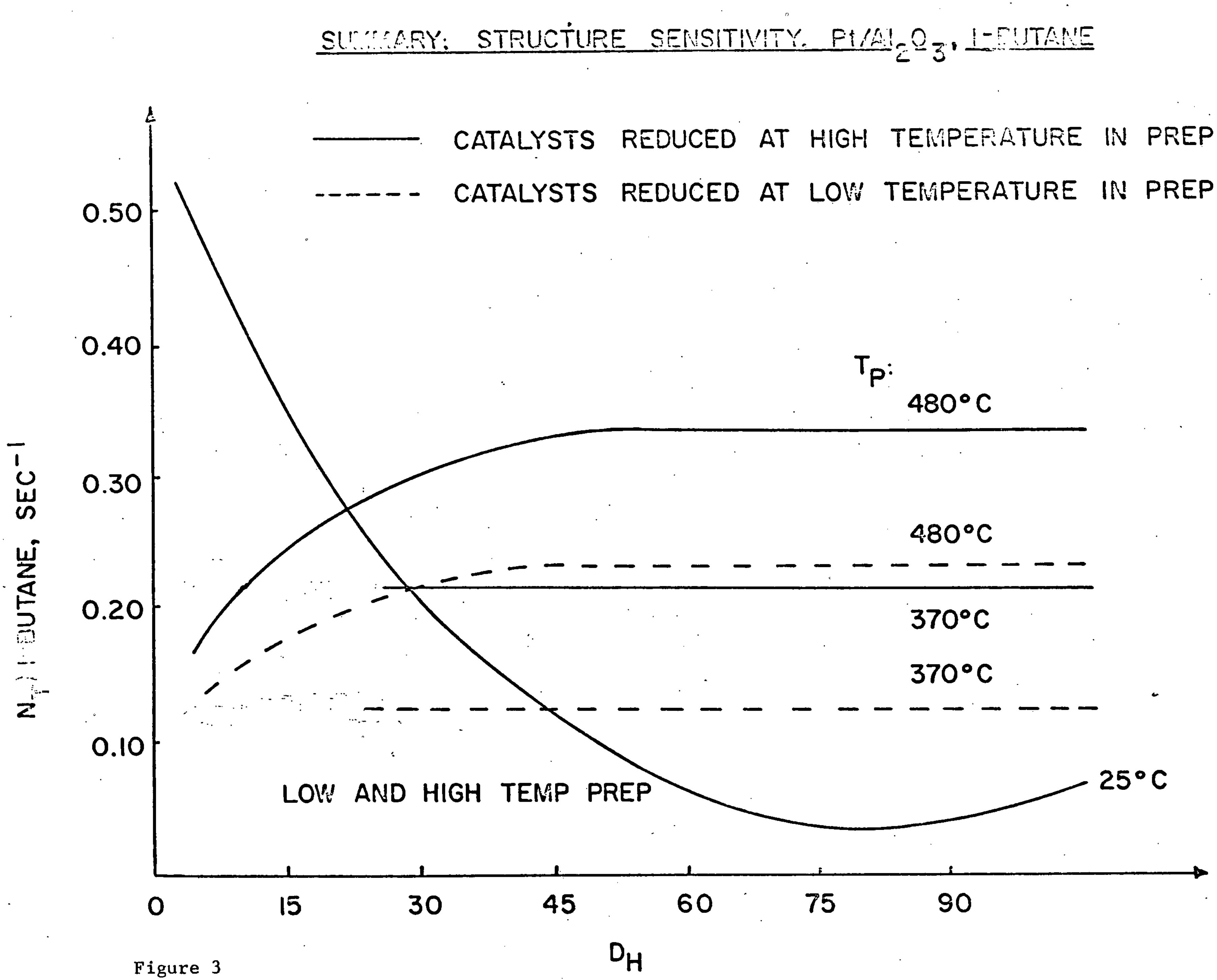

SUMMARY: STRUCTURE SENSITIVITY, Pt/Al$_2$O$_3$, i-BUTANE
CATALYSTS REDUCED AT HIGH TEMPERATURE IN PREP
CATALYSTS REDUCED AT LOW TEMPERATURE IN PREP
T_P:
480°C
480°C
370°C
370°C
25°C
LOW AND HIGH TEMP PREP
0.50
0.40
0.30
0.20
0.10
0
15
30
45
60
75
90
D_H
N_T (i-BUTANE), SEC^{-1}

Figure 3

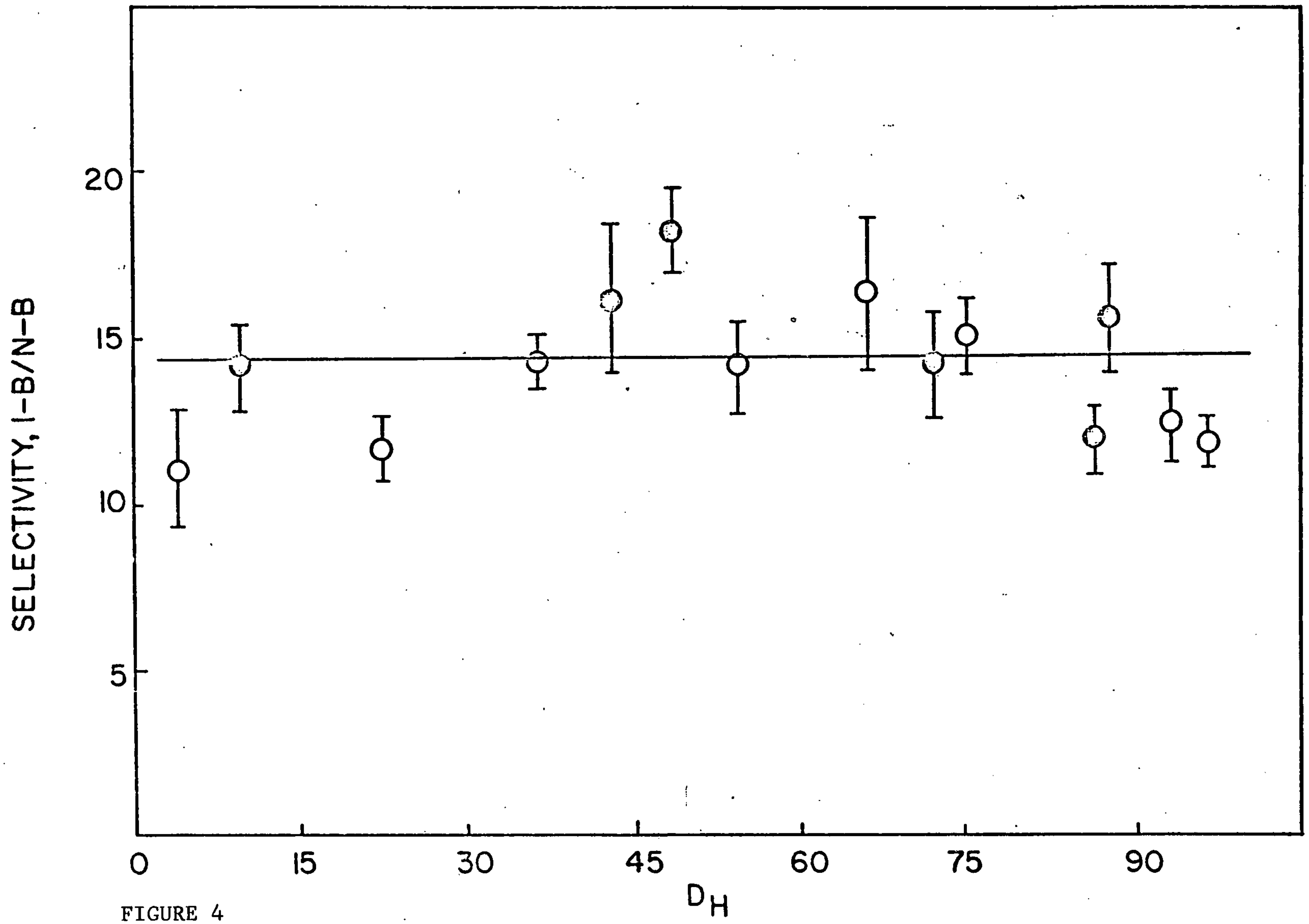


FIGURE 4

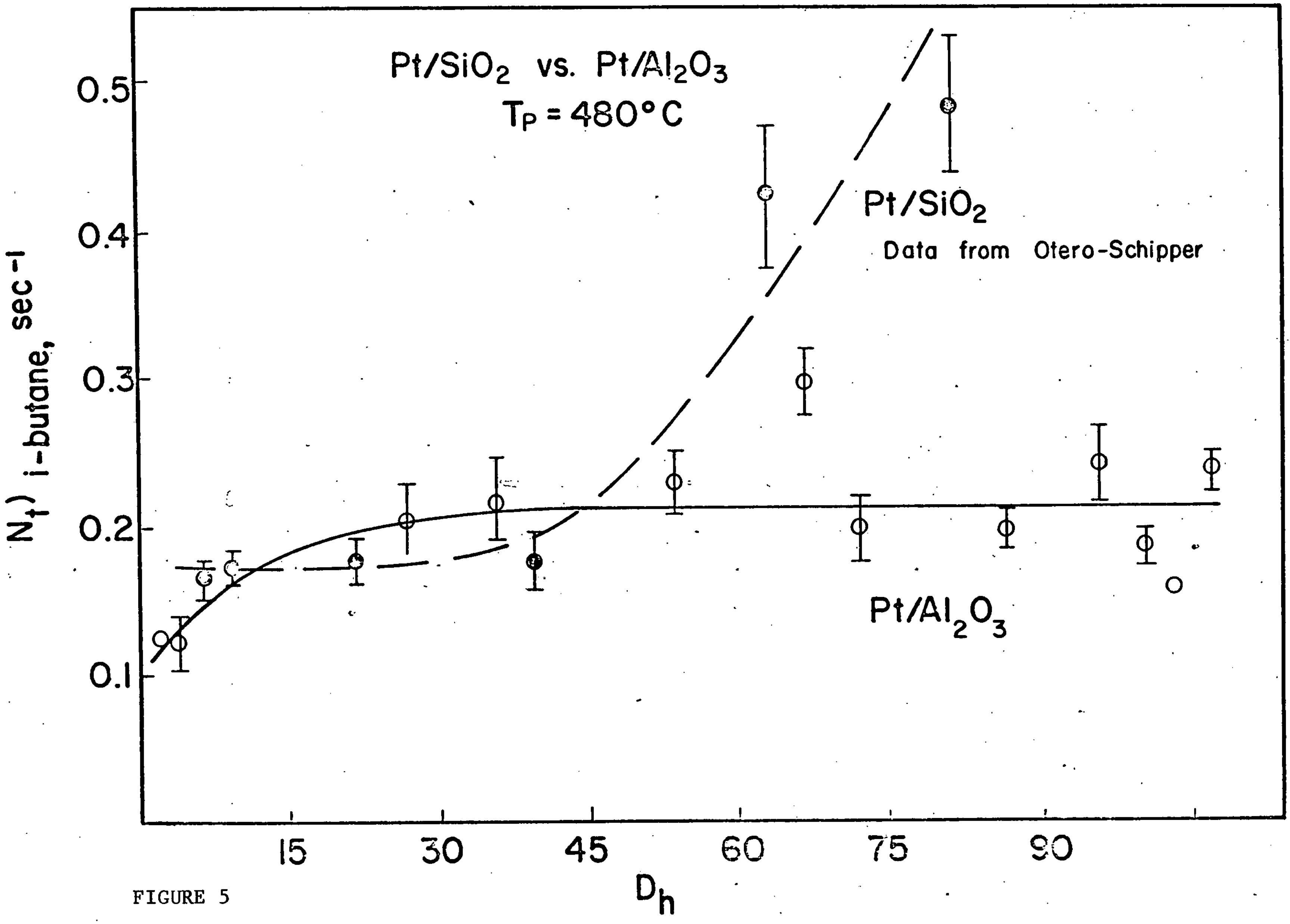
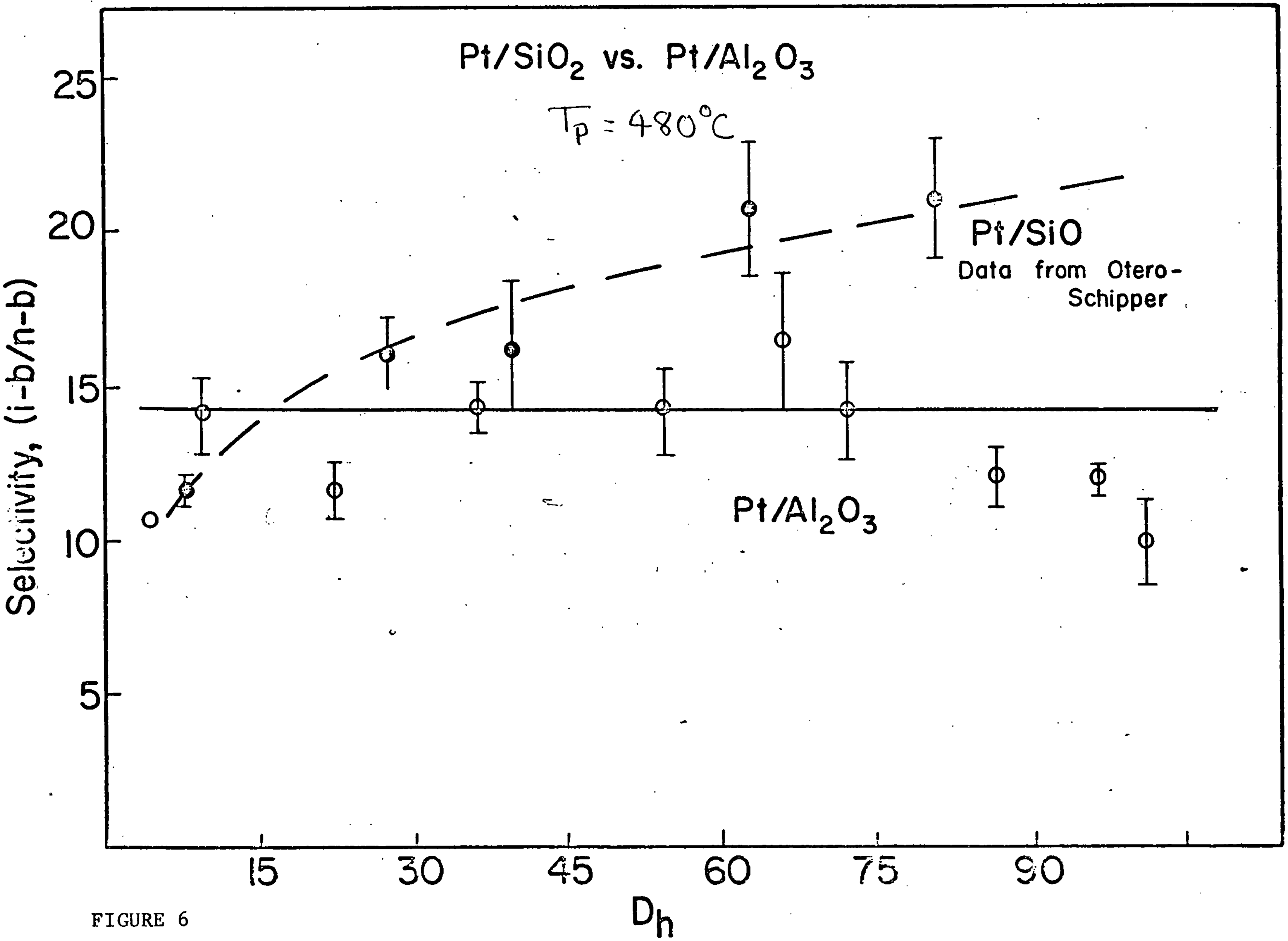

Pt/SiO$_2$ vs. Pt/Al$_2$O$_3$
T_P = 480° C
Pt/SiO$_2$
Data from Otero-Schipper
Pt/Al$_2$O$_3$
$N_t)_{i\text{-butane}}$, sec^{-1}
0.5
0.4
0.3
0.2
0.1
15
30
45
60
75
90
D_h

FIGURE 5

5



Pt/SiO$_2$ vs. Pt/Al$_2$O$_3$
$T_p = 480°C$
Pt/SiO
Data from Otero-Schipper
Pt/Al$_2$O$_3$
Selectivity, (i-b/n-b)
25
20
15
10
5
15
30
45
60
75
90
D$_h$

FIGURE 6

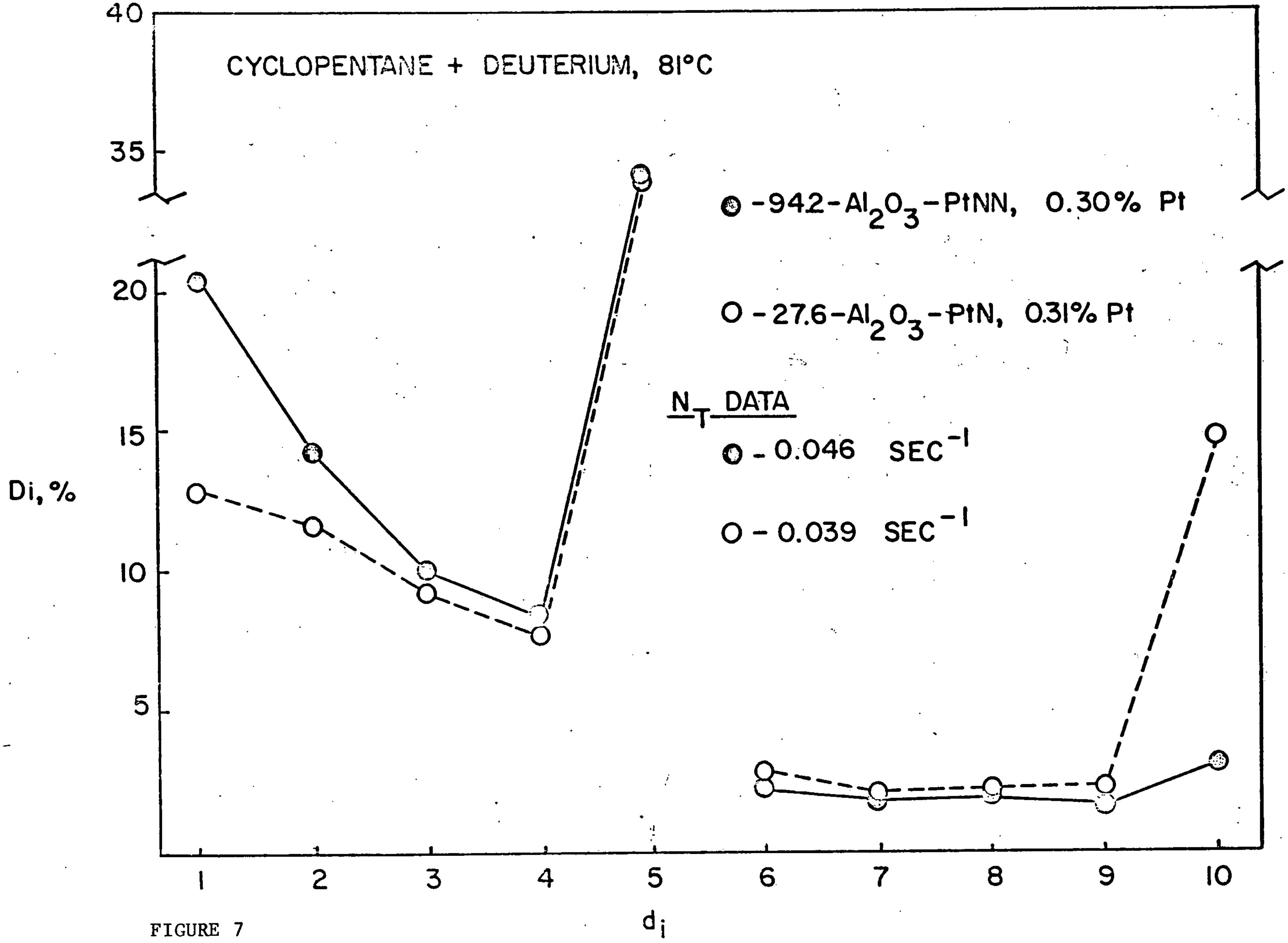

CYCLOPENTANE + DEUTERIUM, 81°C
● -942-Al_2O_3-PtNN, 0.30% Pt
○ -27.6-Al_2O_3-PtN, 0.31% Pt
N_T DATA
● - 0.046 SEC^{-1}
○ - 0.039 SEC^{-1}
Di, %
40
35
20
15
10
5
1
2
3
4
5
6
7
8
9
10
d_i

FIGURE 7

①

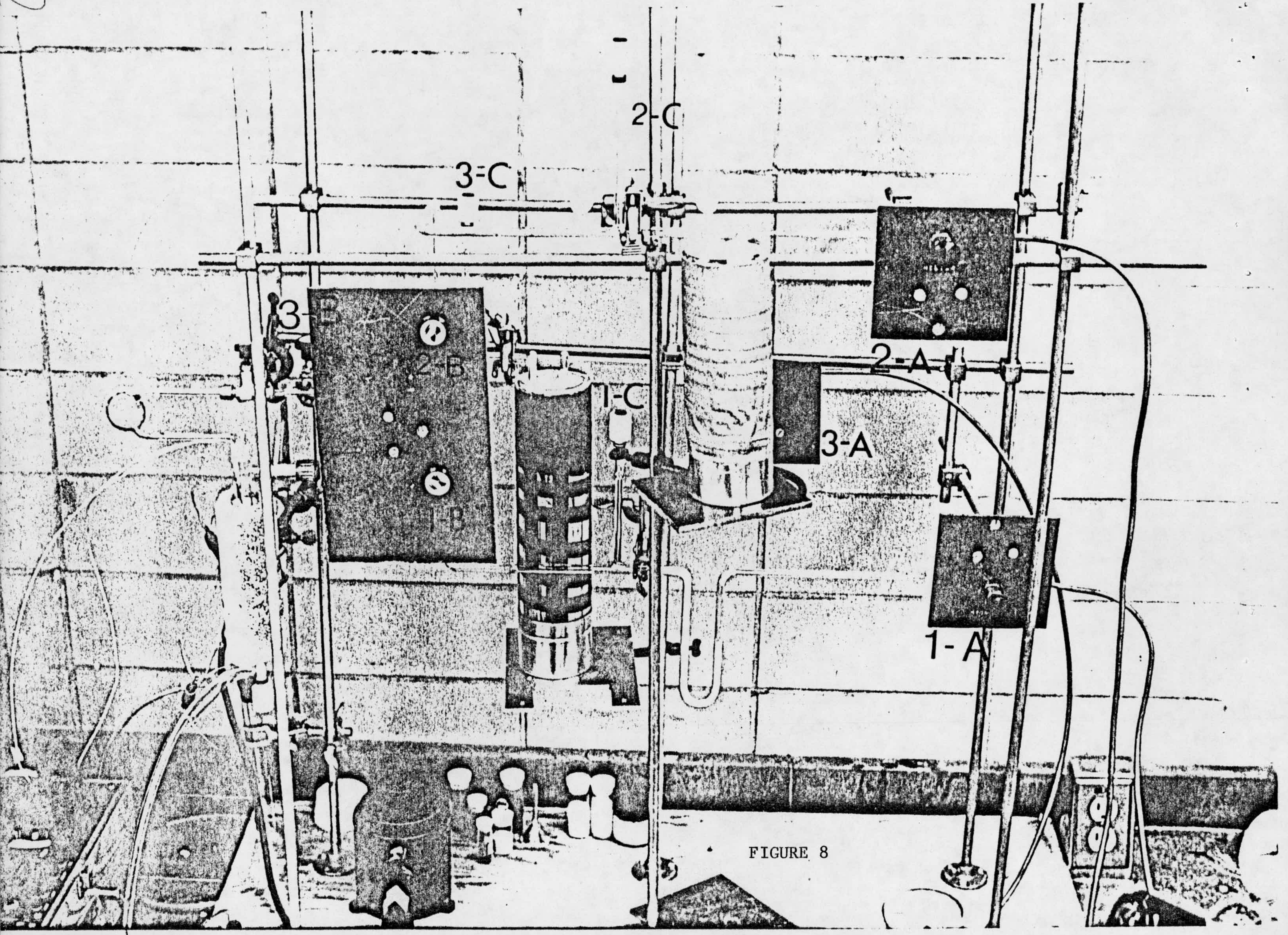


FIGURE 8

To [illegible]

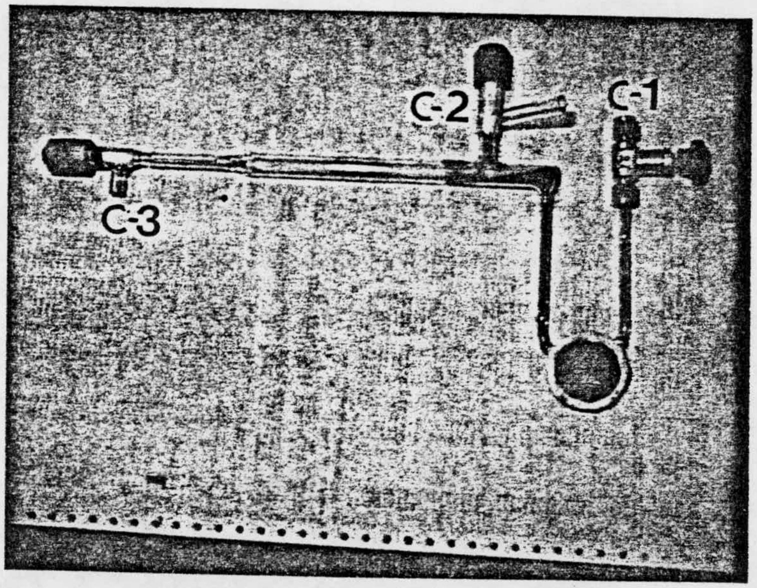


FIGURE 8

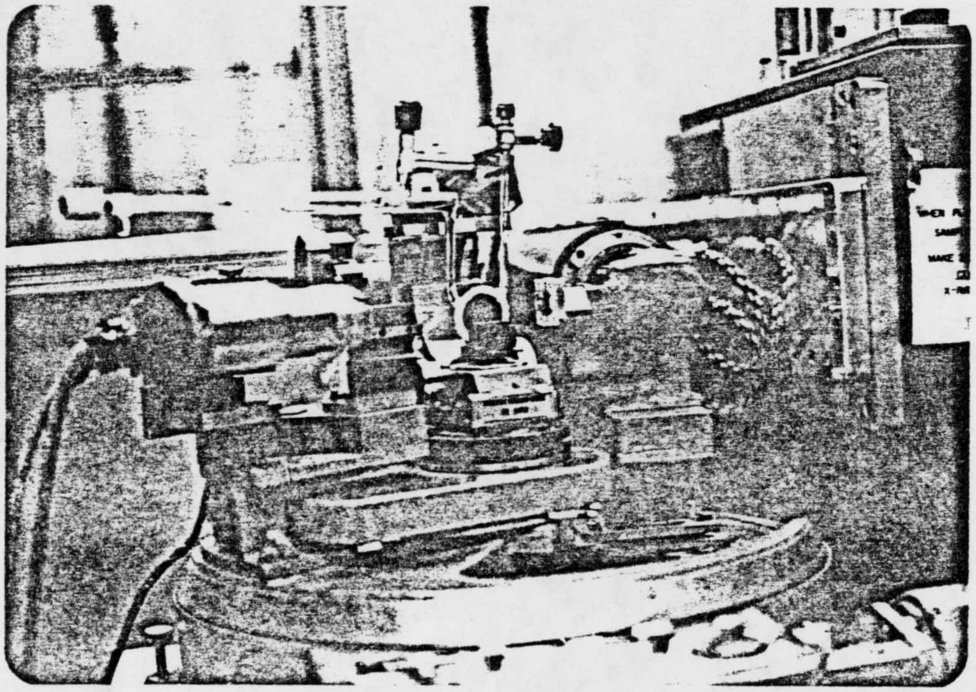


FIGURE 9