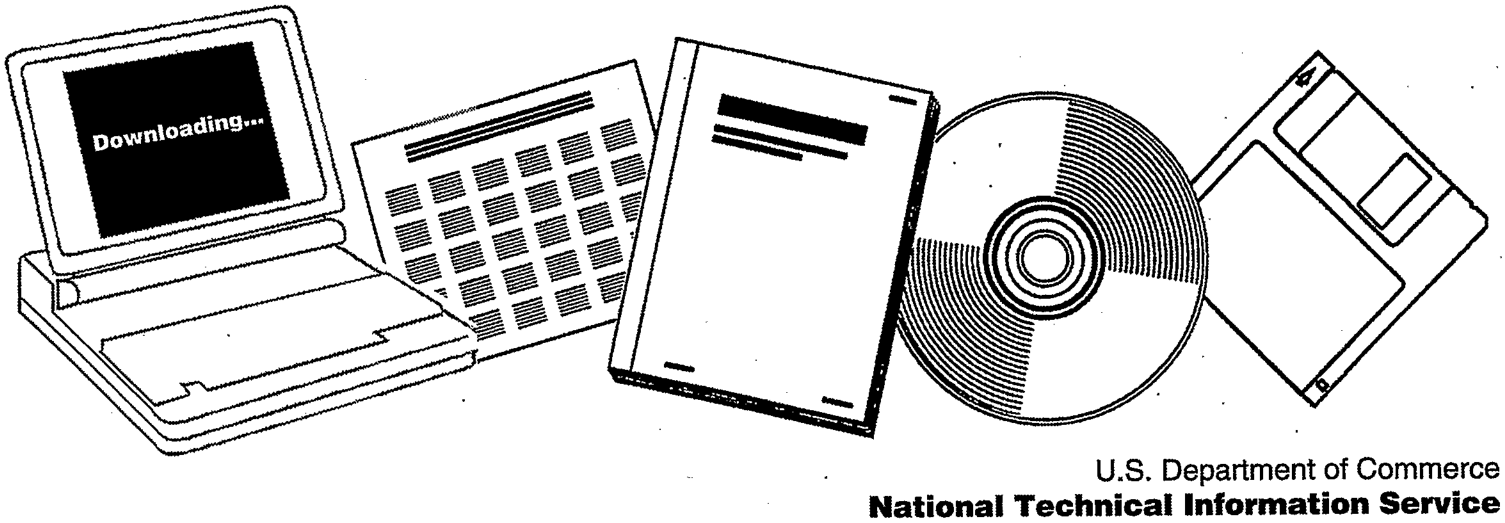
DOEER04463T1

KINETIC AND INFRARED STUDY OF THE EFFECT OF METAL CRYSTALLITE SIZE AND METAL-SUPPORT INTERACTIONS ON CO HYDROGENATION REACTIONS: A THIRD-YEAR PROGRESS REPORT

PENNSYLVANIA STATE UNIV., UNIVERSITY
PARK. DEPT. OF CHEMICAL ENGINEERING

1980



DOE/ER/04463-T1

"A Kinetic and Infrared Study of the Effect of Metal Crystallite Size and Metal-Support Interactions on CO Hydrogenation Reactions"

MASTER

CONTR: PENNSYLVANIA STATE UNIV
OLD PIN: EG-77-S-02-4463
NEW DIN: DE-AS02-77ER04463

A Third-Year Progress Report
to the
Division of Chemical Sciences
Office of Basic Energy Research
U.S. Department of Energy

MASTER

by

M. A. Vannice

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BROOKHAVEN PATENT GROU
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Scope of the Investigation

This program, which began Sept. 1, 1977, has had four major objectives: 1) to examine the effect of metal-support interactions and metal crystallite size on the state of adsorption, on activity, and on selectivity in the CO hydrogenation reaction; 2) to better understand the chemical nature of these effects using chemisorption, x-ray, TEM, kinetic analysis, and infrared spectroscopy; 3) to see if a correlation exists between catalytic behavior and changes in the surface species detected under reaction conditions; and 4) to ultimately develop improved Fischer-Tropsch synthesis catalysts.

To date, the emphasis has been on three metals -- Pt, Pd, and Ni -- because all three have provided evidence indicating sensitivity to a metal-support interaction or a crystallite size effect(1-2). A series of supported catalysts was prepared from each of these metals using alumina, silica, silica-alumina, titania and carbon. These catalysts have been thoroughly characterized by H_2, CO, and O_2 chemisorption, the O_2-H_2 titration reaction, and x-ray line broadening. In addition, transmission electron microscopy (TEM) has been utilized to directly determine particle size distributions in the family of nickel catalysts, with special emphasis being placed on the Ni/TiO_2 catalysts.

We have successfully designed and built a unique IR cell/reactor which operates as a single-pass, differential reactor. This unit has been described in detail in the literature(3). So far, eleven different Pt catalysts and twelve different Pd catalysts have been studied in this program, and all metal/support combinations have been characterized in the ir cell except those on carbon. Kinetic results obtained in this IR cell/reactor have been verified and reproduced in a separate reactor system incorporating a differential, plug-flow reactor which uses ten times the amount of catalyst. These systems and our results are discussed in the next section. These Pt and Pd catalysts have been studied and the influence of SiO_2, Al_2O_3, SiO_2-Al_2O_3, and TiO_2 on CO adsorption has been determined using the unique IR cell designed for this program. This cell operates as a single-pass differential steady-state reactor, provides in situ pretreatment capability, and allows ir spectra and kinetic data to be obtained simultaneously(3). All catalytic results were verified by repeating the kinetic runs in a steady-state microreactor system which utilizes ten times the quantity of catalyst. The ir spectra under reaction conditions have been very informative, quite surprising, and have forced us to consider new kinetic models of the methanation reaction on Pt and Pd because of the absence of large quantities of adsorbed CO on TiO_2-supported Pt and Pd. This modelling work is presently underway.

Significant Results

Platinum and palladium supported on four different oxide materials -- SiO_2, Al_2O_3, SiO_2-Al_2O_3, and TiO_2 -- have been studied in depth. Different preparative techniques were utilized to vary metal particle size and change the state of the metal. For example, Pt and Pd deposited on TiO_2 and reduced at low temperatures (175-200°C) exhibit normal adsorption behavior whereas these same catalysts reduced at a high temperature (500°C) transform into an SMSI (Strong Metal-Support Interaction) state and chemisorption becomes greatly reduced(4). Both fresh and used samples were characterized by H_2, and CO chemisorption. In addition, O_2 chemisorption and the H_2-O_2 titration reaction(5,6) were conducted on most fresh reduced Pt and Pd catalysts to further characterize their adsorption properties and to determine the agreement among these various chemisorption techniques. X-ray line broadening measurements were then conducted on all catalyst samples, and TEM was used to further characterize selected samples, especially the Ni catalysts. Metal loadings were determined by Neutron Activation Analysis.

Tables 1 and 2 provide the chemisorption data on Pt and Pd catalysts respectively, and Tables 3 and 4 show the turnover frequencies (N) measured on Pt and Pd dispersed on various supports. Extensive experiments were conducted to confirm the low N values on Pt/SiO_2 catalysts (Table 5) and the high N values previously reported for Pd/Al_2O_3 catalysts (Table 6). A number of the ir spectra obtained were shown in last year's report and only representative spectra will be attached to this report. However, several of our results are quite noteworthy and typical spectra indicative of these results are shown in Figures 1 through 5. Figure 1 shows the Transmittance spectra for CO adsorbed on SMSI Pt/TiO_2, and it clearly reveals the large reduction in intensity at 300 K when H_2 is added to the system and also shows the very weak band observed under reaction conditions. The difference is remarkable between these spectra and those for the Pt/SiO_2-Al_2O_3 catalyst, which have never been determined previously and are shown in Figure 2. The normal adsorption behavior on Pd/TiO_2 (reduced at 175°C) is shown in Figure 3 along with the complete absence of any ir-active adsorbed CO after the SMSI state has been induced by reduction at 500°C. These spectra can be compared to those in Figures 4 and 5 for CO adsorbed on Pd dispersed on the other supports.

Finally, because we have measured CO adsorption on these catalysts, absolute extinction coefficients can be calculated for the first time for CO adsorbed on these two metals. Our preliminary results are summarized later.

Titania-supported nickel catalysts have been of great interest due to their unusual and improved catalytic properties in the CO hydrogenation reaction(2,7). Five Ni/TiO_2 catalysts with weight loadings of 1.5%, 8%, 10%, 16%, and 30% have been prepared along with 8% Ni/SiO_2 and 8% Ni/Al_2O_3 samples. These reduced catalysts have been thoroughly characterized using H_2, CO, and O_2 chemisorption, x-ray line broadening, and TEM(8). Experiments are now underway with these nickel catalysts to obtain ir spectra under reaction conditions.

Table 7 shows the agreement in average Ni particle size determined from chemisorption, x-ray, and TEM measurements, and Figure 6 shows a typical particle size distribution. For the first time, an adsorption isobar for CO on Ni has been determined and it is shown in Figure 7. Figures 8 and 9 show H_2 adsorption isobars on Ni/SiO_2 and Ni/TiO_2 catalysts. These results clearly show that the low CO and H_2 chemisorption uptakes are not attributable to activated adsorption.

The major results for each of the metals will now be summarized briefly.

A. <u>Platinum</u> -

- Turnover frequencies vary 100-fold, as shown in Table 1, which is a much wider range than that reported previously(1). As with Pd, SMSI Pt/TiO_2 has the highest activity and Pt/SiO_2 has the lowest activity.
- Again, results from the ir reactor and the microreactor agree well.
- Under reaction conditions, surface concentrations of adsorbed CO on Pt/TiO_2 are barely detectable as shown in Fig. 1 -- a result similar to, but not so pronounced as, that for Pd/TiO_2. All other Pt catalysts show strong bands, as shown in Figure 2.

- Unlike Pd, the HF species dominates on Pt surfaces.
- Extinction coefficients have also been calculated for these Pt catalysts. That for Pt/SiO_2 based only on a ratio of peak heights is in excellent agreement with earlier values determined by Eischens(9) and by Tompkins(10). Our average integrated extinction coefficients of 1×10^{-18} $molecule^{-1}$ cm^2 are the first reported for Pt. Surprisingly, these values have not yet been often determined for Group VIII metals.
- These Pt catalysts have been thoroughly characterized by H_2, CO, and O_2 chemisorption, the H_2-O_2 titration at 300 K, and x-ray line broadening. Preparative variables have been studied to allow dispersions to be altered 50-fold without requiring high temperature sintering steps.
- H_2 competes with CO much more effectively for sites on SMSI Pt/TiO_2, and substantial CO displacement occurs at 300 K. The higher activity may be due to this effect.

B. <u>Palladium</u>

- Turnover frequencies vary by a factor of 40, as shown in Table 2, and confirm previous results of Vannice. TiO_2-supported Pd is most active and SiO_2-supported Pd is least active.
- Agreement between kinetic results from ir cell, microreactor, and previous work is extremely good.
- Little or no ir-active CO exists on the TiO_2-supported SMSI Pd catalyst under reaction conditions. This is an unusual result and is the first report of an active CO hydrogenation catalyst that does not have chemisorbed CO as the predominant surface species. All other Pd catalyst show strong bands during reaction.

- When visible, the low frequency (LF) band predominates over the high frequency (HF) band (Figures 3-5). This LF band is normally associated with bridged- or multiply-bonded CO whereas the HF band is associated with linearly adsorbed CO. Equilibrium CO adsorption in the absence of H_2 has been studied by ir, and no CO bands are observed for SMSI Pd/TiO_2 at 300 K either, as shown in Figure 3.
- For the first time, absolute ir extinction coefficients have been calculated for CO adsorbed on Pd. In addition, separate extinction coefficients have been estimated for the HF and LF species, and the latter has an average value about an order of magnitude greater than that for the HF species (7×10^{-16} molecule^{-1} cm^{2} vs 3×10^{-17} molecule^{-1} cm^{2}).
- Chemisorption experiments have shown that three different H_2 adsorption techniques agree reasonably well among themselves and with CO uptakes. However, the H_2-O_2 titration reaction at 373 K reproducibly gives H_2 uptakes that are ~15% high.

c. Nickel

- Good agreement was obtained among average crystallite sizes on SiO_2 and Al_2O_3 calculated from three different techniques: H_2 and CO chemisorption, x-ray line broadening, and TEM.
- For Ni/TiO_2 catalysts, H_2 and CO chemisorption measurements indicated crystallite sizes far larger than those determined by x-ray and TEM; however, the sizes measured by O_2 chemisorption were in excellent agreement with the sizes determined by the last two techniques assuming an adsorption stoichiometry of $O/Ni_s = 1$.

- Oxygen chemisorption on TiO_2-supported nickel appears to be decreased compared to that normally occurring on large Ni crystallites.
- Isobars for CO and H_2 have shown that activated adsorption is not the cause of decreased monolayer coverages on TiO_2-supported nickel.
- Transmission electron micrographs show evidence for 2-dimensional, "pill box" particles similar to those observed by the Exxon workers for Pt on TiO_2(11).

Level of Activity

My major effort has been devoted to this program. It has required a third of my time, and it has been very productive and informative. I believe it is worthy of maintenance at this level.

One of the students involved in this program, Joe S. Smith, has completed his Masters Degree. His thesis is entitled "The Crystallite Size Distribution and Adsorption Behavior of Titania-Supported Nickel". One of the Ch.E. seniors has been studying H_2, O_2, and CO chemisorption and the O_2-H_2 titration reaction on supported Pd catalysts.

Two Ph.D. students, one of whom is self-supporting, are completing the work on their theses. One should finish by Fall Term and the other should complete his work during Fall Term.

Although no changes in objectives are perceived, some new directions in research have become apparent as a result of our work to date. First, ir spectra obtained during transient experiments, such as step changes in CO or H_2 concentrations, can provide much information about the relative adsorption bond strength of the different CO species. A small, heated ir cell with a very small dead volume should be constructed -- this would allow experiments with rapid response times to be conducted at different temperatures. Also, the results of this research have emphasized the importance of differences in heats of adsorption and in heats of interaction between different adsorbed species -- CO and H_2 in this system. Such data are not available in the literature and their values are important from both a fundamental and a practical viewpoint. This is especially true for characterization of the SMSI catalysts. For example, monolayer coverage at 773 K by <u>strongly-adsorbed</u> hydrogen on Pt/TiO_2 has been proposed as the reason for low uptakes at 300 K(12) rather than low monolayer coverages of hydrogen due to weak adsorption caused by a metal-support interaction(13).

Publications

Four publications have already resulted from this work, and these are listed below. Copies have been attached to the accompanying Renewal Proposal. One additional publication has been submitted to the J. of Catalysis describing Joe Smith's thesis research, and four manuscripts on the Pt and Pd catalysts are in preparation. At least two of these should be completed by the end of August.

The publications are:

1. M. A. Vannice, S. H. Moon, C. C. Twu, and S-Y. Wang, J. Phys. E:Sci. Instru. <u>12</u>, 849 (1979). "A Design for a Combined Infrared Cell/Differential Single-Pass Reactor".
2. M. A. Vannice, T. R. Kiliany, and M. B. Palmer, Jr., React. Kinet. Catal. Lett. <u>12</u>, 321 (1979). The Consistency of Repeated H_2-O_2 Titration Cycles on Supported Pt Catalysts".

3. M. A. Vannice, S. H. Moon, and C. C. Twu, ACS Preprints - Petr. Chem. Div. 25, 303 (1980). "A Simultaneous IR/Kinetic Study of Supported Platinum Methanation Catalysts".
4. M. B. Palmer, Jr. and M. A. Vannice, J. Chem. Tech. Biotechnol. 30, (1980). "The Effect of Preparation Variables on the Dispersion of Supported Pt Catalysts".

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1. M. A. Vannice, J. Catal. 40, 129 (1975).
2. M. A. Vannice and R. L. Garten, J. Catal. 56, 236 (1979).
3. M. A. Vannice, S. H. Moon, C. C. Twu, and S-Y. Wang, J. Phys.E:Sci. Instru. 12, 849 (1979).
4. S. J. Tauster, S. C. Fung and R. L. Garten, J. Am. Chem. Soc. 100, 170 (1978).
5. J. E. Benson and M. Boudart, J. Catal. 4, 704 (1965).
6. J. E. Benson, H. S. Hwang and M. Boudart, J. Catal. 30, 146 (1973).
7. M. A. Vannice and R. L. Garten, J. Catal., Accepted for Publication.
8. J. S. Smith, M.S. Thesis, Pennsylvania State University (1980).
9. R. P. Eischens and W. A. Pliskin, Adv. Catal. 10, 1 (1958).
10. H. Heyne and F. C. Tompkins, Tr. Faraday Soc. 63, 1274 (1967).
11. R. T. K. Baker, E. B. Prestridge and R. L. Garten, J. Catal. 56, 390 (1979).
12. S. C. Fung, S. J. Tauster, R. T. K. Baker, J. A. Horsley, and R. L. Garten, Paper 94, 179th ACS National Meeting, Houston, TX, March, 1980.
13. P. G. Menon, Personal Communication following Paper 117, 179th ACS National Meeting, Houston, TX, March, 1980.

Table 1

H_2 and CO Adsorption on Fresh Pt Catalysts

Catalyst	CO Uptake (μmole g^{-1})	H_2 Uptake (μmole g^{-1})	CO/Pt	H/Pt
2.1% Pt/η-Al_2O_3	--	52	----	0.96
2.0% Pt/η-Al_2O_3	--	12.5	----	0.24
1.5% Pt/SiO_2 (D)	13	6.5	0.17	0.17
1.3% Pt/SiO_2	--	14.0	----	0.42
[A] 2% Pt/TiO_2 (200C)	9	6.7	0.09	0.13
[A] 2% Pt/TiO_2 (500C)	--	----	----	----
1.5% Pt/SiO_2-Al_2O_3	--	28	----	0.72

2/11/80

Table 2

H_2 and CO Adsorption on Fresh Pd Catalysts

Catalyst	CO Uptake (µmole g^{-1})	H_2 Uptake (µmole g^{-1})	CO/Pd	H/Pd
2% Pd/η-Al_2O_3	83	38	0.44	0.40
2% Pd/SiO_2 (D)	26	18	0.14	0.19
2% Pd/SiO_2-Al_2O_3	59	27	0.31	0.28
2% Pd/TiO_2 (175C)	41	16	0.22	0.17
2% Pd/TiO_2 (500C)	12	0 29(a)	0.06	0

a) Total H_2 Uptake

2/11/80

Table 3

Specific Activity of Pt Catalysts

$P = 101$ kPa, $T = 548$K, $H_2/CO = 3$

Catalyst	$N_{CH_4} \times 10^3$ (molecules CH_4 $site^{-1}s^{-1}$)$^{(a)}$		
	IR Cell	Reactor	Previous Work
2.1% Pt/η-Al_2O_3 (0.96)	0.9	1.3, 1.6	1.2(b)
2% Pt/η-Al_2O_3 (0.24)	1.6	2.1	---
1.5% Pt/SiO_2 (D)	ND	0.12	
1.3% Pt/SiO_2	---	0.07	0.55(b)
1.5% Pt/SiO_2-Al_2O_3	1.1	0.6	---
[A] 2% Pt/TiO_2 (200C)	8.5	4.9, 6.2	---
[A] 2% Pt/TiO_2 (500C)	6.2	11, 28	---
[A] 2% Pt/TiO_2 (500C)	0.80(c)	1.4, 3.6(c)	3.1(c)

a) Based on $H_{(ad)}$ on fresh catalyst

b) M. A. Vannice, J. Catal. 40, 129 (1975)

c) Based on 100% dispersion

2/11/80

Table 4

Specific Activity of Pd Catalysts

$P = 101$ kPa, $T = 548$K, $H_2/CO = 3$

Catalyst	$N_{CH_4} \times 10^3$ (molecules site^{-1} s^{-1})(a)		
	IR Cell	Reactor	Previous Work
2% $Pd/\eta\text{-}Al_2O_3$ (e)	3.3	4.8	7.4, 12
2% Pd/SiO_2 (D)	ND	0.12	0.32
2% $Pd/SiO_2\text{-}Al_2O_3$	1.9	----	----
2% Pd/TiO_2 (175C)	2.0	4.1(b),4.6(b)	----
2% Pd/TiO_2 (500C)	6.5(b)	12(b), 17(b)	----
2% Pd/TiO_2 (500C)	0.39(c)	0.7(c) 1.0(c)	0.53(c)
2% Pd/TiO_2 (500C)	1.8(d)	3.1(d),4.6(d)	----

a) Based on CO adsorption on used sample

b) Based on CO adsorption on fresh sample

c) Assuming 100% Dispersion

d) Based on CO adsorption on fresh (175C) sample

3/7/80

Table 5

Silica-Supported Pt Has Low Activity

Catalyst	$N_{CH_4} \times 10^3$ (a) (s^{-1} @ 548K)	H/Pt (a)
1.5% Pt/Davison	0.12	0.17
1.3% Pt/COS	0.07	0.42
2.0% Pt/COS (I)	0.06	0.63
2.0% Pt/COS (E)	0.08	1.0
2.1% Pt/Al_2O_3	2	0.96
2% Pt/TiO_2 (200C)	6	0.13

a) Based on H_2 adsorption on fresh catalyst

2/11/80

Table 6

Turnover Frequencies for Pd/Al_2O_3 Catalysts

(molecule·site^{-1}·s^{-1}) @ 101 kPa, 548K

Catalyst	$N_{CH_4} \times 10^{3}$ (a)	E_{CH_4} (kcal mole^{-1})	CO/Pd (a)
2% Pd/η-Al_2O_3 (i)	8.8	19.4	0.065
2% Pd/η-Al_2O_3 (e)	4.8	20.1	0.12
2% Pd/η-Al_2O_3 (e)(c)	4.6	13.8	0.23
2% Pd/η-Al_2O_3 (c)	12	19.7	0.11
2% Pd/η-Al_2O_3 (c & s)	7.4	23.6	0.067
9.5% Pd/η-Al_2O_3 (c & s)	10	21.0	0.043
10% Pd/η-Al_2O_3 (c & s)	5.1	22.2	0.034
10% Pd/η-Al_2O_3 (s)	8.5	19.2	0.019

a) Based on CO adsorption on used catalyst

2/11/80

Table 7

AVERAGE PARTICLE SIZES

Catalyst	$\bar{d}_s$ (nm)				$\bar{d}_v$ (nm)	
	H_2	CO	O_2	TEM[a]	X-Ray	TEM[a]
8% Ni/TiO_2	25	19	8[b]	8	10	9
16% Ni/TiO_2	21	23	5[b]	9	9	10
8% Ni/SiO_2	6	6	6[c]	11	10	14
8% $Ni/\eta\text{-}Al_2O_3$	6	6	5[c]		10	

a - all TEM results are mean values.
b - assuming $O/Ni_s = 1$.
c - assuming $O/Ni_s = 2$.

IR Spectra of CO Adsorbed on 2% Pt/TiO_2 (500C)

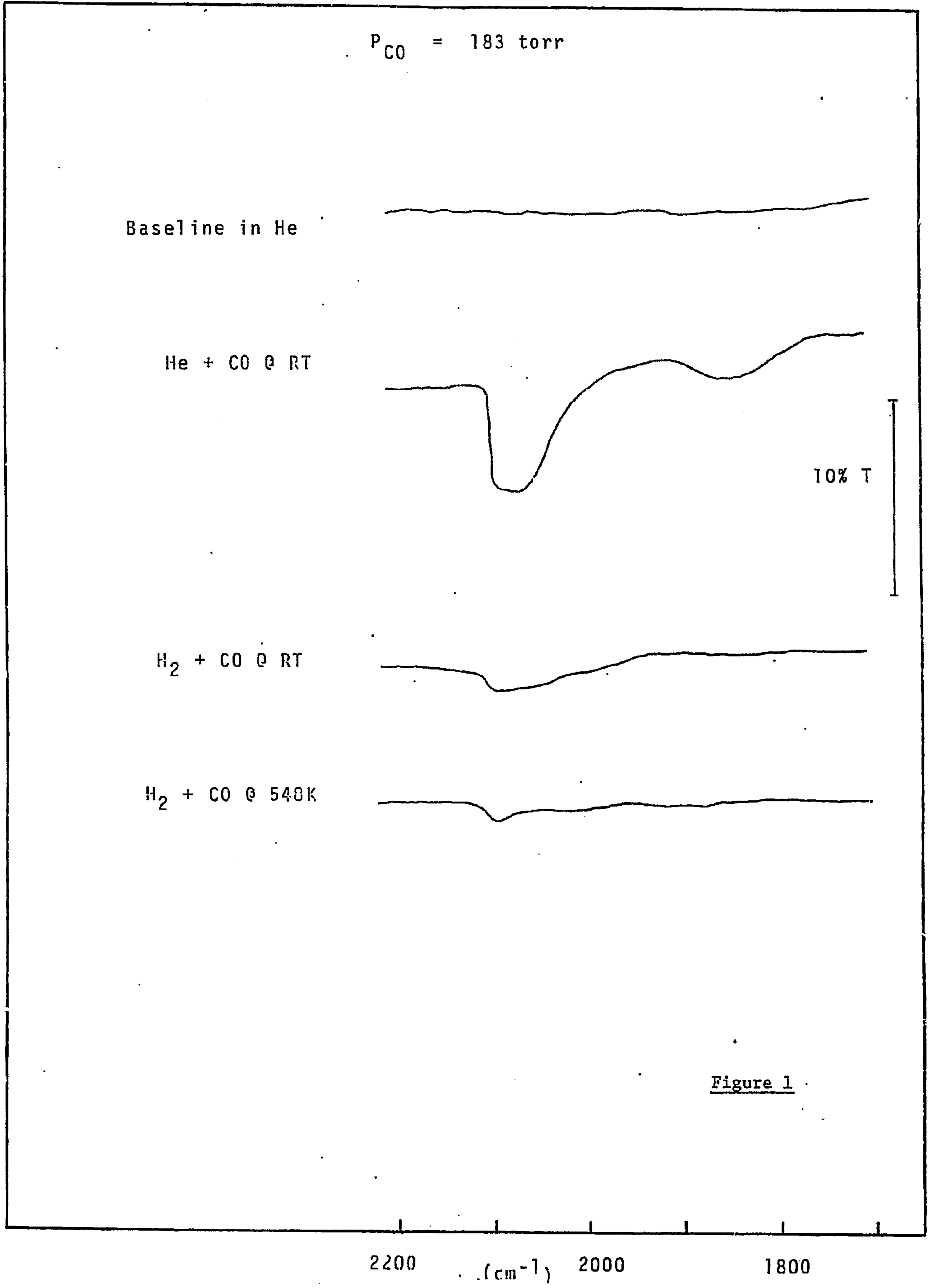
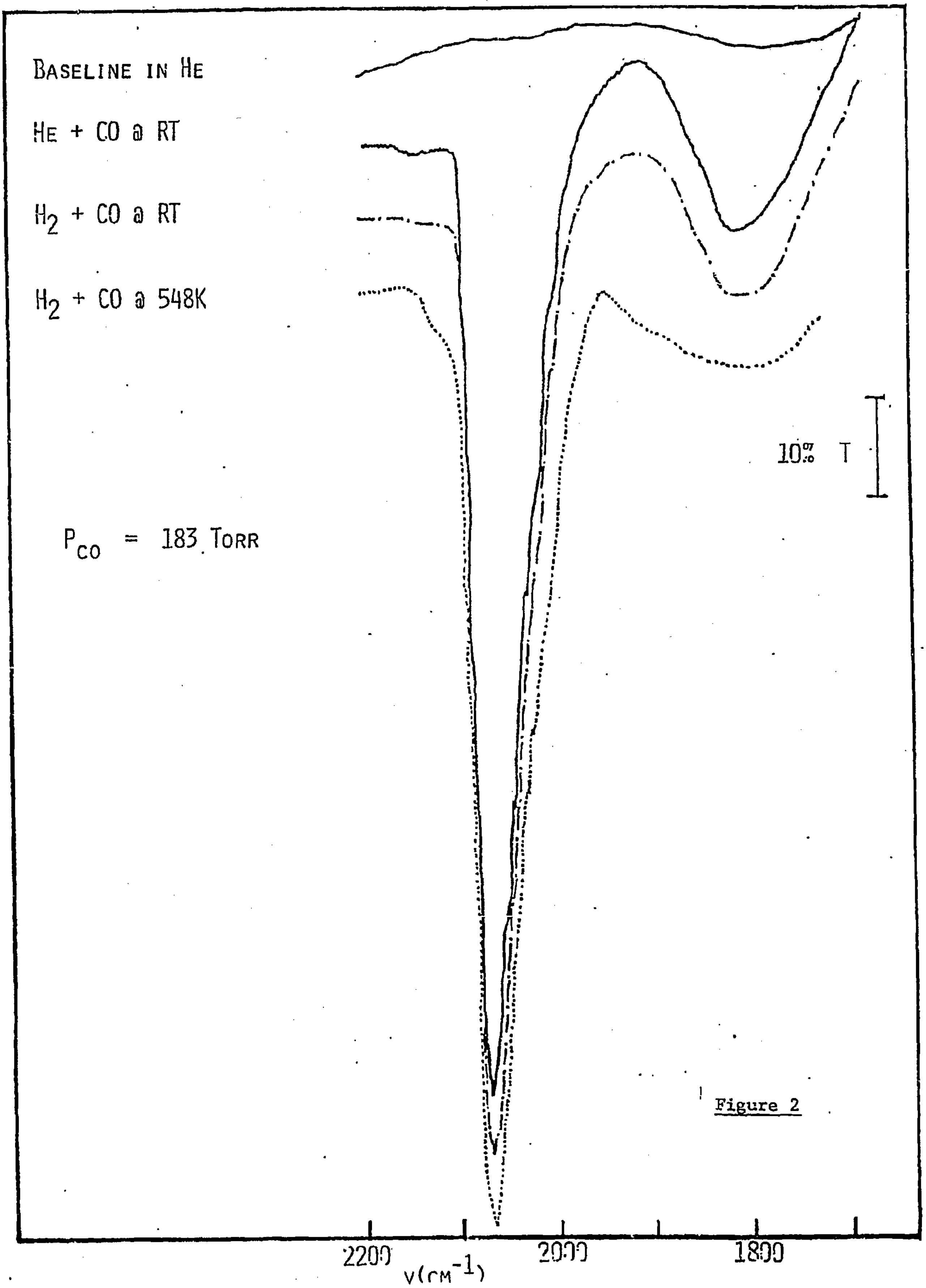


Figure 1



IR Spectra of CO Adsorbed on 1.5% $Pt/SiO_2-Al_2O_3$

Figure 2

IR SPECTRA OF CO ADSORBED ON 2% PD/TiO_2

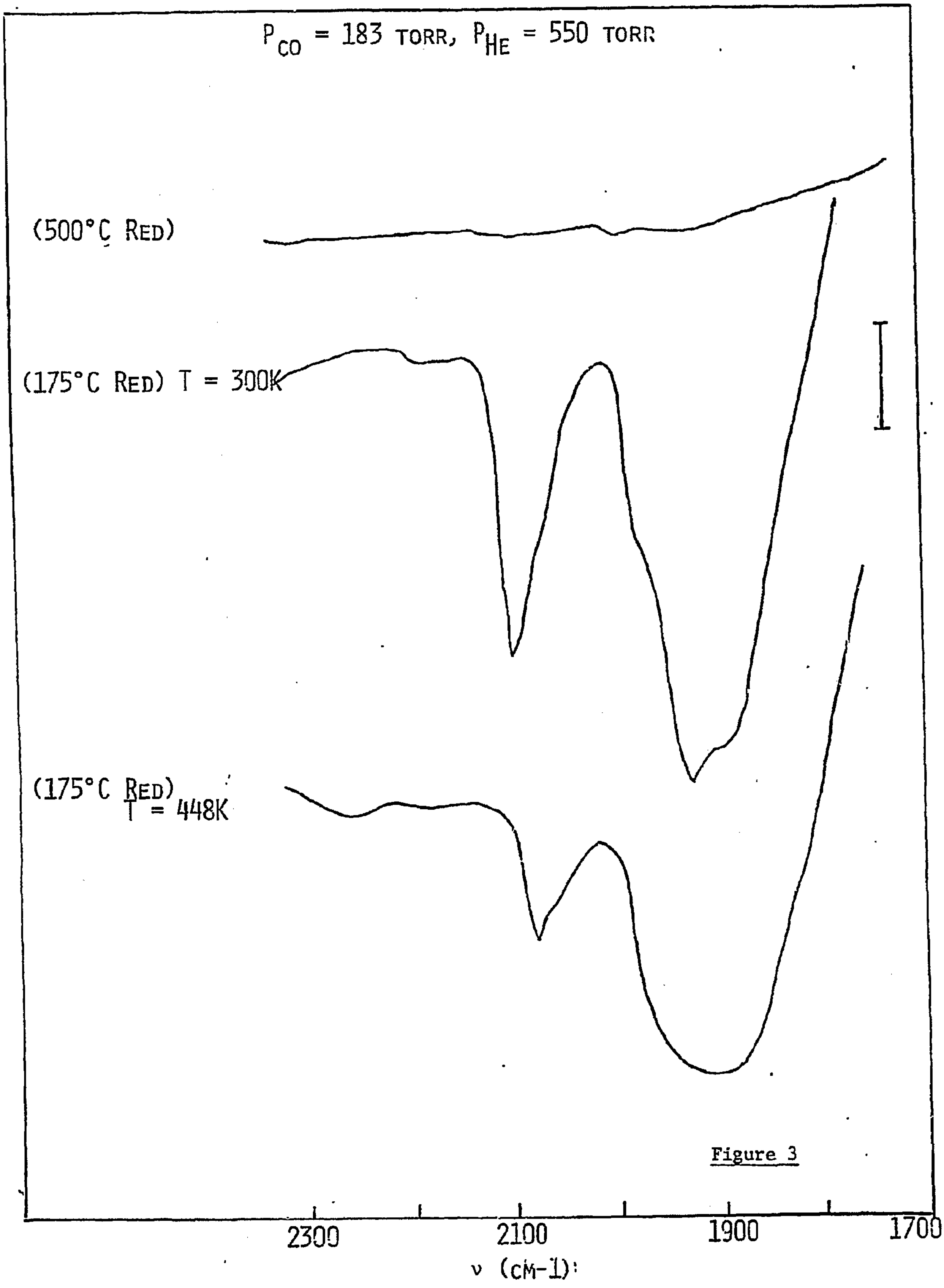
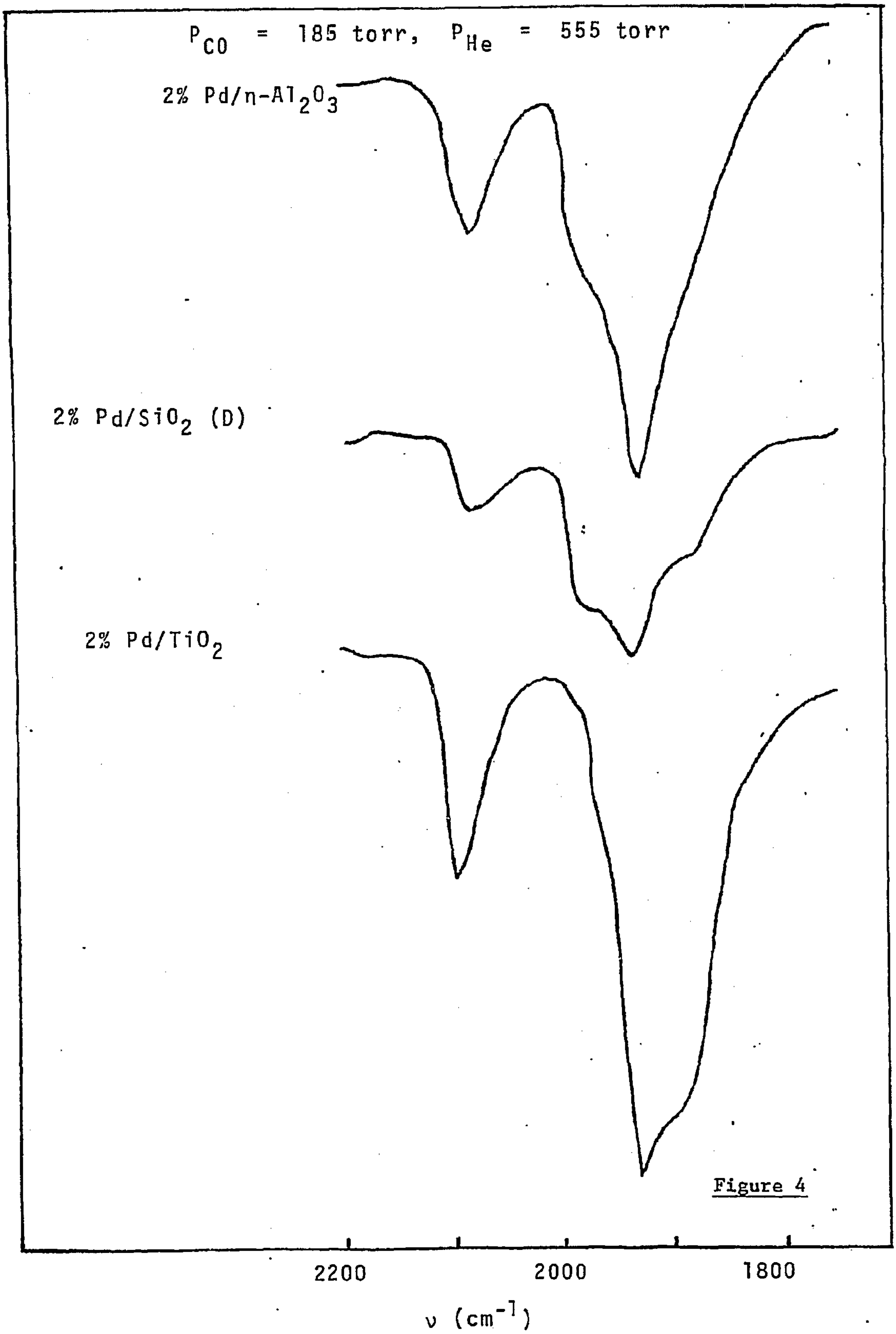


Figure 3



IR Spectra of CO Adsorbed on Pd at 300K

Figure 4

CO ADSORBED ON 2% $Pd/SiO_2-Al_2O_3$

P_T = 101 kPa, He/CO = 3

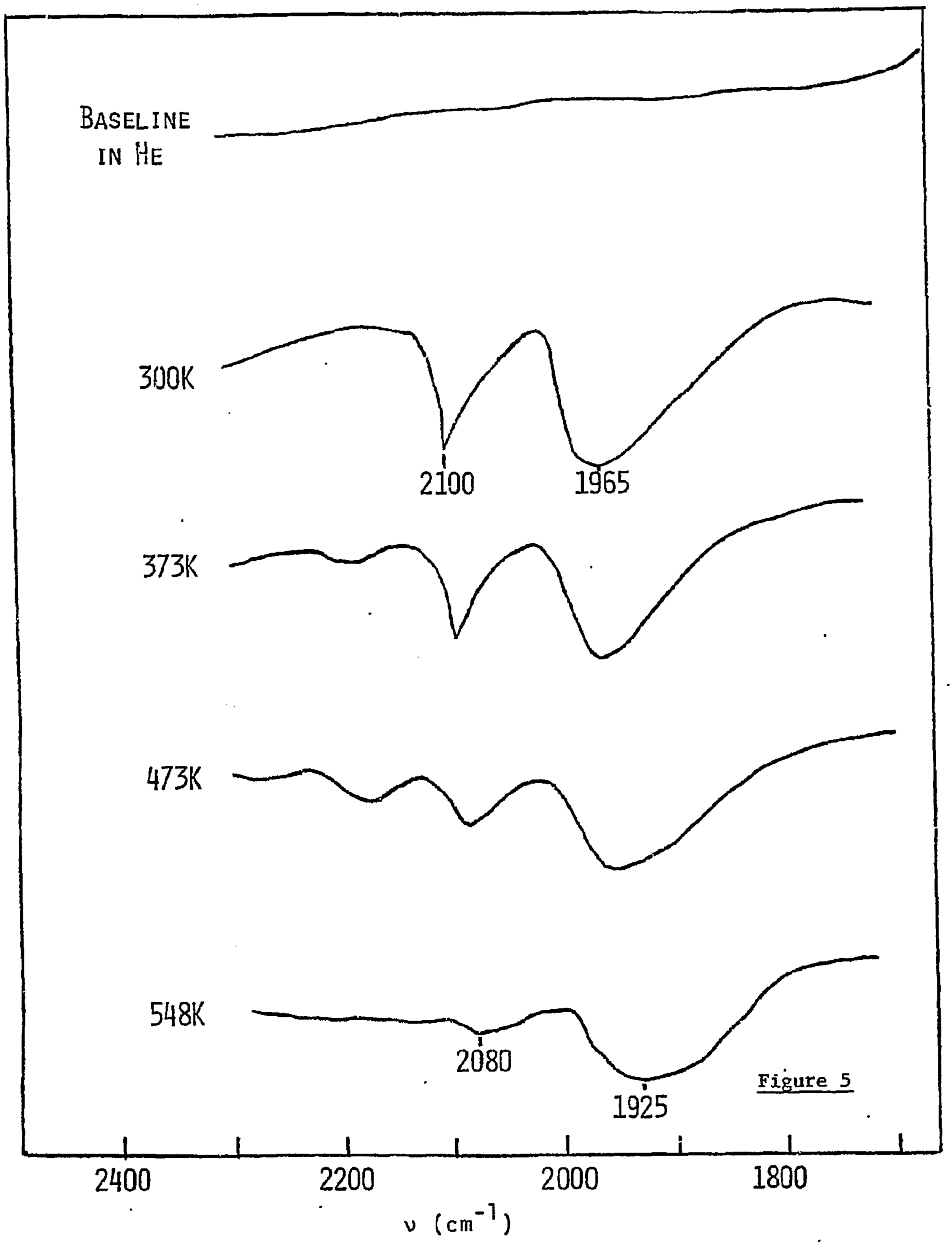


Figure 5

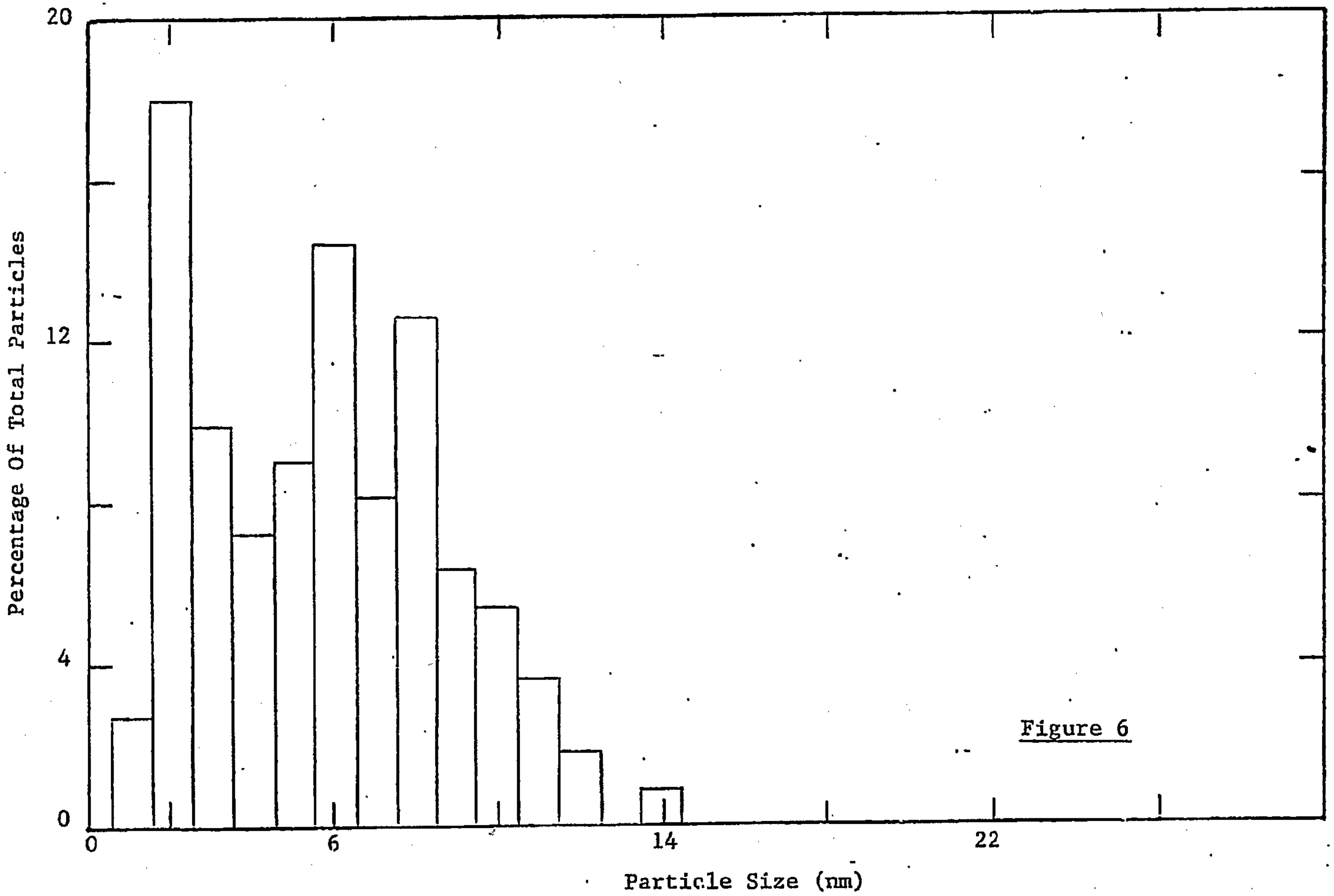
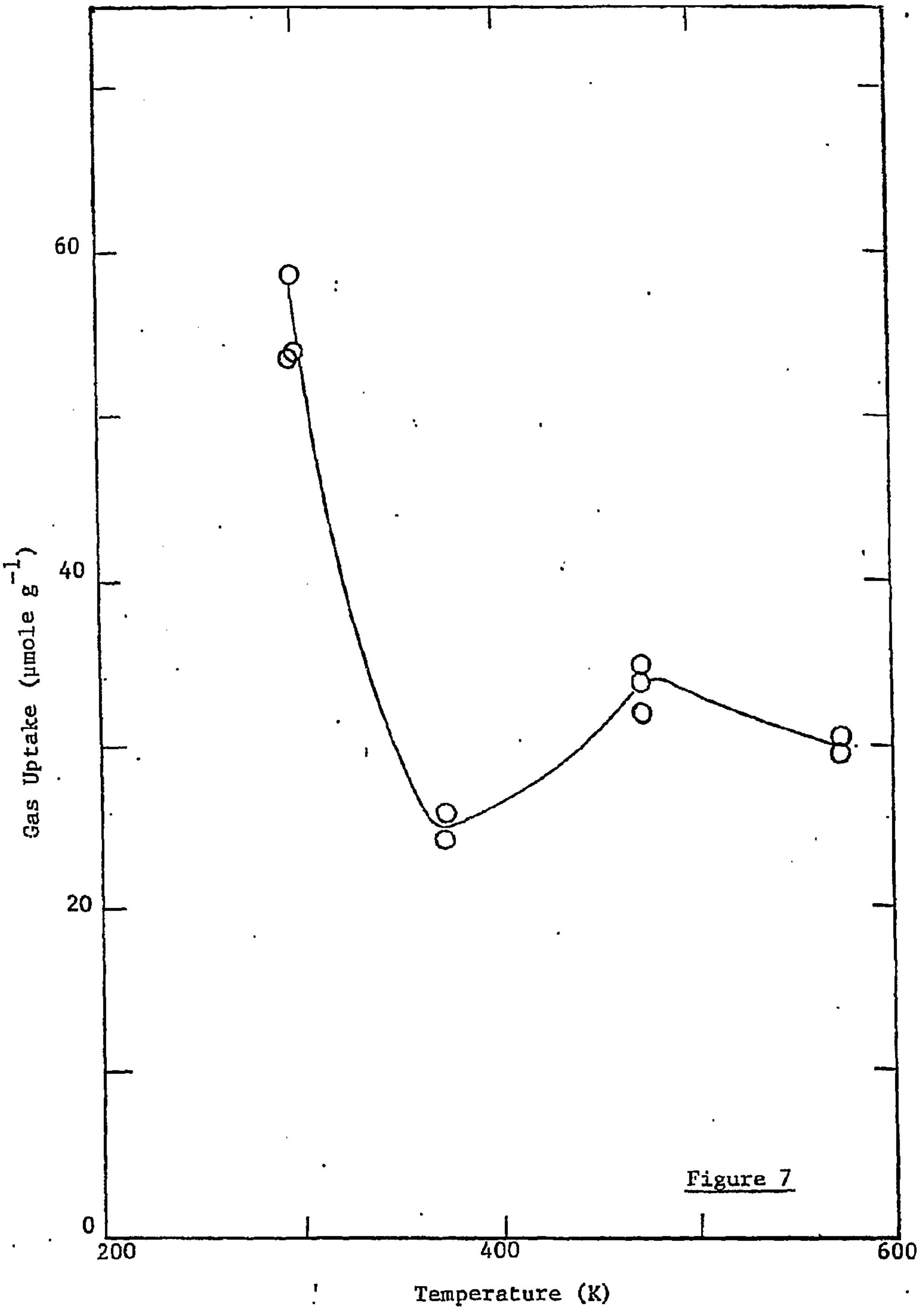
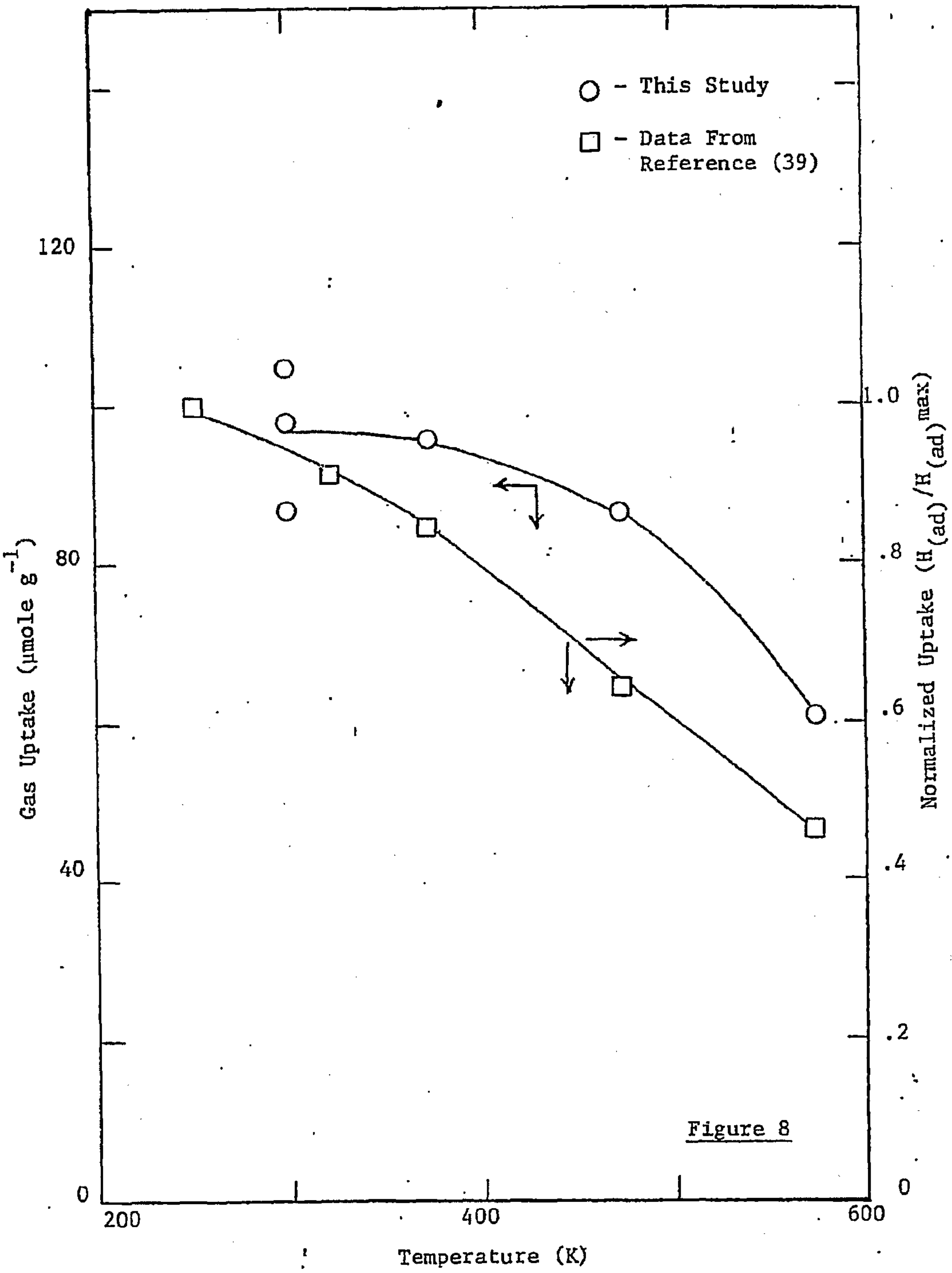


Figure 6

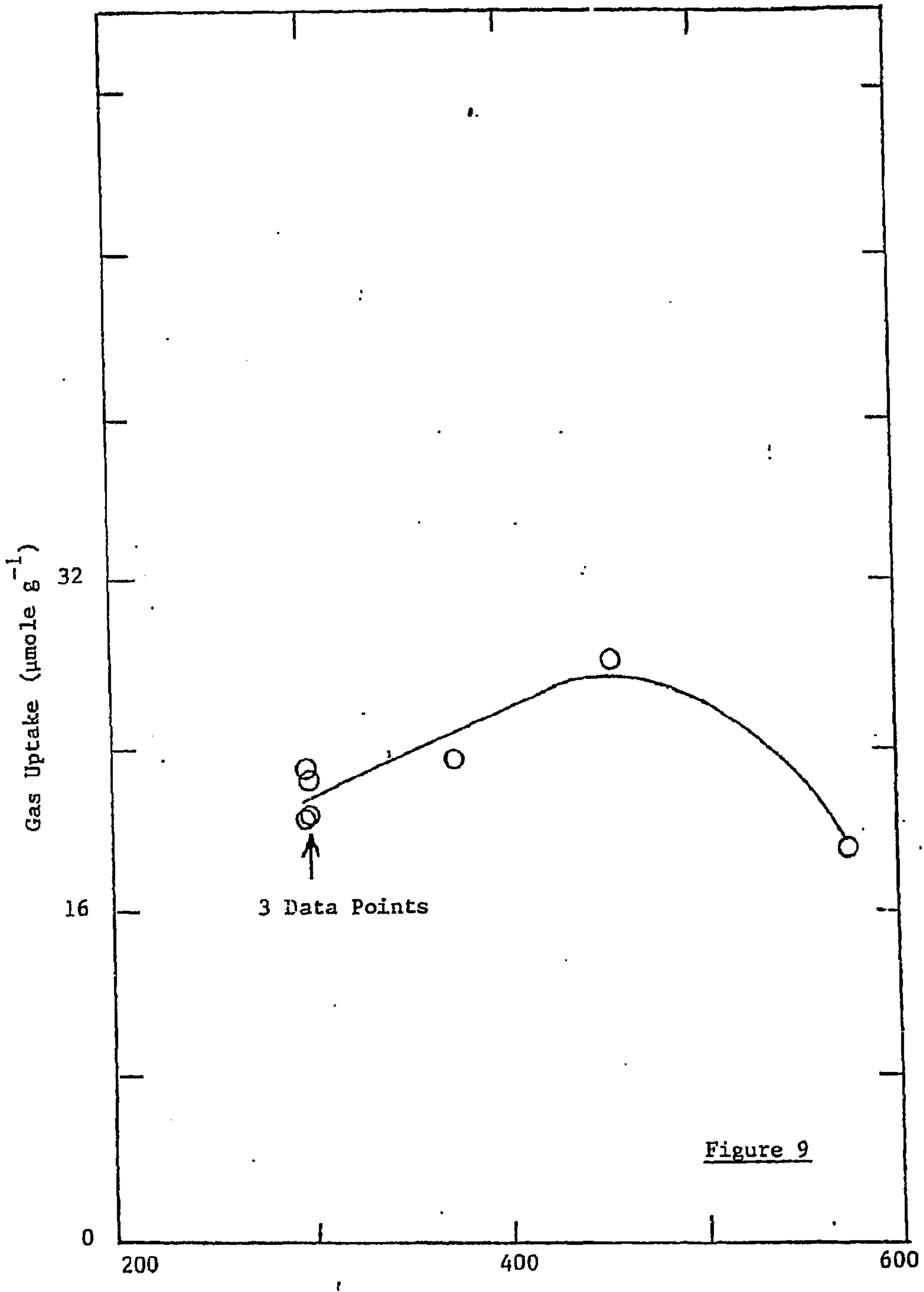
PARTICLE SIZE DISTRIBUTION FOR 8% Ni/TiO_2



CO ISOBAR FOR 8% Ni/TiO_2



H_2 ISOBAR FOR 8% Ni/SiO_2



H_2 ISOBAR FOR 8% Ni/TiO$_2$