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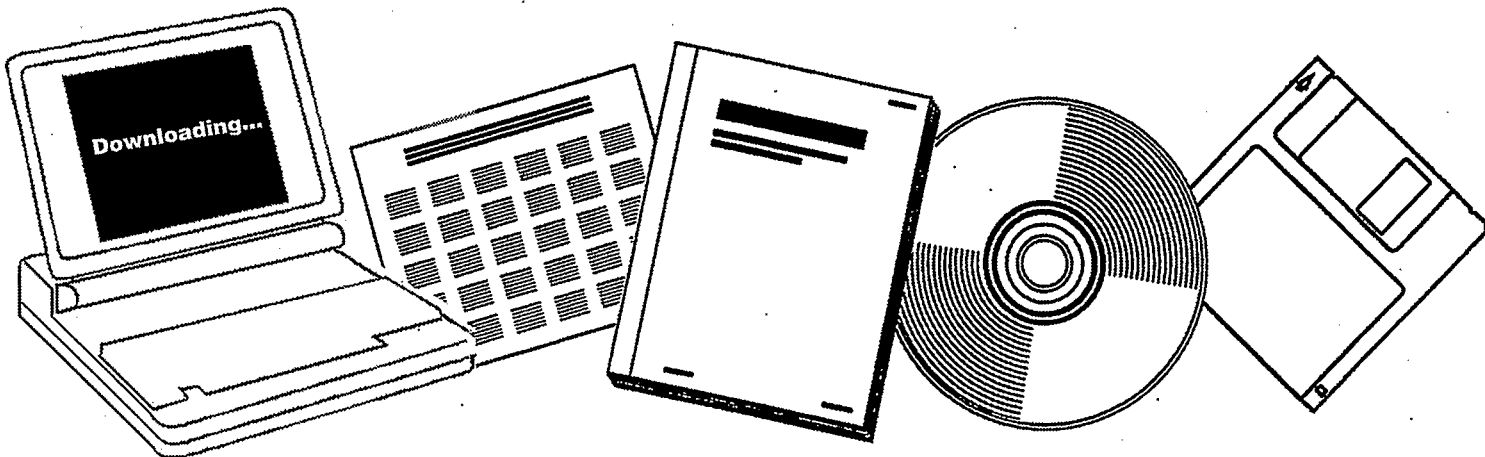
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**CHARACTERIZATION OF CATALYSTS WITH
METAL-SUPPORT EFFECTS AND OF THE SPECIES
ADSORBED ON THEIR SURFACES. PROGRESS
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CHARACTERIZATION OF CATALYSTS WITH METAL-SUPPORT EFFECTS
AND OF THE SPECIES ADSORBED ON THEIR SURFACES

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Research Efforts

During the past year we have succeeded in modifying our DSC-2C calorimeter to greatly enhance its sensitivity and stabilize the baseline behavior. The details of the changes required have been given in a recent publication (1). As a result we have extensively studied the influence of crystallite size and the support on heats of adsorption of H_2 , CO , and O_2 on Pt and Pd. The results for Pt are shown in Tables 1 and 2 and Figures 1 and 2, and are summarized briefly as follows.

Isothermal, integral heats of adsorption have been measured for H_2 and CO adsorption on Pt dispersed on four supports. These values were determined at 215K and 300-320K using our modified differential scanning calorimeter. At room temperature $\Delta H_{(ad)}$ for H_2 ranged from 21 to 36 kcal/mole on the "typical" Pt catalysts, which included Pt/ TiO_2 (LTR) reduced at 473K. The heats of adsorption were highest on Pt/ SiO_2 and lowest on Pt/ TiO_2 (LTR); however, a clear trend existed between $\Delta H_{(ad)}$ and Pt fraction exposed, with large Pt crystallites having the highest values, as shown in Figure 1. A high temperature reduction (HTR) at 773K of Pt/ TiO_2 markedly decreased both chemisorption capacity and the heat of adsorption, with values as low as 5-10 kcal/mole occurring after repeated HTR cycles. These results provide direct evidence that a decrease in the H-Pt bond strength can be at least partially responsible for lower chemisorption capacity; however, migration of TiO_x species onto the Pt is assumed to cause physical blockage of some Pt sites as well as modification of the chemical properties of the few remaining surface Pt atoms that are available for adsorption. A linear correlation exists between the logarithm of the CH_4 turnover frequency and the H_2 heat of adsorption. This study is reported in detail elsewhere (1,2).

The Pt catalysts which had "normal" CO adsorption behavior exhibited a range of $\Delta H_{(ad)}$ values for CO between 21 and 32 kcal/mole at 300K, with the more poorly dispersed Pt/SiO₂ catalysts having the highest values and the very highly dispersed Pt/TiO₂ (LTR) samples, reduced at 473K, the lowest values. As with H₂, a consistent trend occurred under "normal" adsorption conditions, independent of support, that indicated the presence of a crystallite size effect, with weaker CO-Pt bonding occurring on small Pt crystallites (Figure 2). Only the Pt/TiO₂ samples after a high temperature reduction (HTR), which showed the decreased chemisorption capacity associated with the "SMSI" state, exhibited a pronounced support effect which reduced heats of adsorption at 300K after repeated HTR cycling to values as low as 10 kcal/mole CO. All $\Delta H_{(ad)}$ values were lower at 215K, and the range between 15-20 kcal/mole on the "normal" catalysts indicated the filling of lower-energy states. Again the logarithm of the CH₄ turnover frequency (TOF) correlated almost linearly with the CO heat of adsorption over a 1000-fold variation in specific activity. However, this enhancement in TOF cannot be easily explained by considering only a decrease in CO and H₂ $\Delta H_{(ad)}$ values and is attributed to the presence of special active sites at the Pt-support interface. This investigation has been discussed in recent papers (2,3).

For supported Pd, a range of $\Delta H_{(ad)}$ values for H₂, CO, and O₂ were obtained, as indicated in Table 3 and shown in Figures 3-5. The integral $\Delta H_{(ad)}$ values for CO and O₂ were in excellent agreement with initial values obtained in UHV systems, while those for H₂ were consistently 5-10 kcal/mole higher than those reported in UHV studies. The Pd catalysts exhibited behavior different than that for the Pt catalysts in two major aspects. First, $\Delta H_{(ad)}$ values tended to increase somewhat as crystallite sizes became very small, particularly in the region below 6 nm where crystallite size

effects are expected to be most pronounced. Second, the high temperature reduction (HTR) step did not decrease the $\Delta H_{(ad)}$ values as significantly for Pd/TiO₂. This indicates that generalizations about "SMSI" behavior are difficult to make, even among the noble metals. Some of these data have recently been reported (4).

In addition, because our experimental method routinely involved the formation and decomposition of β -phase Pd hydride, we have measured its enthalpy of formation. Our values, which are consistently near 20 kcal/mole H₂ for both supported Pd and ultrapure Pd powder, are double those reported in the literature. We attribute this discrepancy to reporting errors in the earlier studies, which inadvertently listed values per mole H rather than per mole H₂.

Presently, a range of Pt crystallite sizes on SiO₂ and on η -Al₂O₃ are being prepared to better ascertain the crystallite size effect on heats of adsorption. Also, the results from extensive kinetic studies of benzene hydrogenation over Pd catalysts are being analyzed to provide a detailed catalytic model for this reaction.

References

1. M. A. Vannice, L. C. Hasselbring, and B. Sen, J. Catal., In press.
2. M. A. Vannice, L. C. Hasselbring, and B. Sen, J. Phys. Chem., In Press.
3. M. A. Vannice, L. C. Hasselbring, and B. Sen, J. Catal., Sub. for Pub.
4. M. A. Vannice and P. Chou, JCS Chem. Comm., 1984, 1590.

Personnel and Publications

Two PhD students are currently working on this program, one of whom will be completing his thesis this fall.

The following publications, sponsored by this DOE program have appeared

in print during the past year:

1. Vannice, M. A. and Chou, P., "The Influence of Pretreatment and the Support on Benzene Hydrogenation over Pd", Proc. 8th Int. Cong. on Catalysis, V-99, DECHEMA, Frankfurt, 1984.
2. Vannice, M. A., Leong, T. and Sudhakar, C., "Methanation Over Supported Pt Catalysts", ACS Prepr., Div. Petr. Chem. 29, 558 (1984).
3. Vannice, M. A. and Sudhakar, C., "A Model for the Metal-Support Effect ~~Enhancing CO-Hydrogenation Rates Over Pt-TiO₂ Catalysts~~", ~~J. Phys. Chem.~~ 88, 2429 (1984).
4. Vannice, M. A. and Chou, P., "Heats of Adsorption of H₂ and CO on a Pd/TiO₂ "SMSI" Catalyst", JCS Chem. Comm., (1984), 1590.

The following papers have not yet appeared in the literature:

1. Vannice, M. A., Hasselbring, L. C., and Sen, B., "Direct Measurements of Heats of Adsorption on Pt Catalysts. I. H₂ on Pt Dispersed on SiO₂, Al₂O₃, SiO₂-Al₂O₃, and TiO₂," J. Catal., In Press.
2. Vannice, M. A., Hasselbring, L. C., and Sen, B., "Metal-Support Effects on H₂ and CO Heats of Adsorption on TiO₂-Supported Pt," J. Phys. Chem., In Press.
3. Vannice, M. A., Hasselbring, L. C., and Sen, B., "Direct Measurements of Heats of Adsorption on Pt Catalysts. II. CO on Pt Dispersed on SiO₂, Al₂O₃, SiO₂-Al₂O₃, and TiO₂," J. Catal., Sub. for Publication.

TABLE 1

HEATS OF ADSORPTION OF HYDROGEN ON SUPPORTED PLATINUM

Catalyst	Sample	Weight (mg)	Pre-treatment	Adsorption Temperature (°K)	No. of Runs	Average Energy Change, ΔH (mcal/g)	ΔH (ad)		
							(a) (kcal/mole)	(b)	
2.1% Pt/ η -Al ₂ O ₃	I	60.6	A	320	2	1109	---	27.8 ± 1.1	
		215	A	215	4	617	14.8 ± 0.5	12.8 ± 0.4	
	II	62.7	A	320	3	1003	---	25.1 ± 0.7	
		215	A	215	4	601	14.4 ± 0.5	12.5 ± 0.4	
	1.5% Pt/SiO ₂ -Al ₂ O ₃	I	32.3	A	320	2	439	---	29.1 ± 1.9
		II	34.5	A	320	4	415	---	27.5 ± 2.5
2.1% Pt/SiO ₂	I	33.7	A	320	2	148	---	36.1 ± 6.9	
	II	36.9	A	215	2	48	7.4 ± 1.7	5.7 ± 1.2	
2.1% Pt/SiO ₂	II	36.9	A	300	3	421	---	27.7 ± 3.0	
	III	37.3	A	320	5	313	---	34.4 ± 4.7	
1.5% Pt/TiO ₂ (LTR)	I	40.6	B*	320	3	807	---	21.0 ± 0.7	
	II	99.5	B*	215	3	373	14.6 ± 0.6	12.2 ± 0.5	
2.0% Pt/TiO ₂ (LTR)	I	98.4	B	300	3	818	---	25.7 ± 0.9	
		98.4	B	300	4	854	---	27.1 ± 2.3	
	IIA(c)	98.4	B	300	4	524.4	---	22.8 ± 3.1	
		91.8	B	300	2	1049.6	---	21.1 ± 0.5	
	III	106.2	B	300	4	868.0	---	27.6 ± 3.6	
		106.2	B	300	4	595.5	---	25.9 ± 3.7	
1.5% Pt/TiO ₂ (HTR)	I	41.4	C	320	1	8.5	---	5.7	
	II	64.5	C	320	3	4.5	---	3.0 ±	
2.0% Pt/TiO ₂ (HTR)	I	108.6	C*	300	4	13.8	---	13.8 ± 12.2	
		98.4	C*	300	3	16.3	---	10.4 ± 10.5	
	IIA(c)	98.4	C*	300	3	13.9	---	9.9 ± 4.4	
		106.2	C*	300	3	16.4	---	10.3 ± 5.2	
	IV	106.2	C*	300	4	27.2	---	19.4 ± 8.1	
		106.2	C*	300	4	27.2	---	19.4 ± 8.1	

(a) Based on irreversible adsorption on Pt.

(b) Based on total adsorption on Pt.

(c) A indicates values obtained after treatment in 20% O₂/80% He at 673K for 30 min followed by an LTR or HTR step, as listed in the Table.

(W) Water-treated catalyst.

TABLE 2

HEATS OF ADSORPTION OF CARBON MONOXIDE ON SUPPORTED PLATINUM

Catalyst	Sample	Weight (mg)	Pre- treatment	Ads. Temp (°K)	No. of Runs	Average Energy Change (mcal/g)	$\Delta H_{(ad)}$ (kcal/mole)	
2.1% Pt/ η -Al ₂ O ₃	I	60.6	A	320	3	1162	23.7 ± 0.7	
			A	215	4	1174	15.2 ± 0.4	
	II	62.7	A	320	2	1178	24.0 ± 0.2	
			A	215	2	1231	16.0 ± 0.1	
1.5% Pt/SiO ₂ -Al ₂ O ₃	I	32.3	A	320	3	613	23.1 ± 0.6	
			A	215	3	583	19.4 ± 0.7	
2.1% Pt/SiO ₂	I	33.7	A	320	2	324	27.0 ± 2.5	
			A	215	2	225	16.7 ± 1.7	
2.1% Pt/SiO ₂ (W)	II	36.9	A	300	2	672	27.5 ± 2.5	
	III	37.3	A	320	4	514	31.7 ± 3.2	
1.5% Pt/TiO ₂ (LTR)	I	40.6	B*	320	1	1059	20.2	
			B**	320	2	1049	20.0 ± 0.5	
			B*	215	2	675	10.9 ± 0.5	
2.0% Pt/TiO ₂ (LTR)	I	A(c)	108.6	B	300	2	691	21.6 ± 0.9
	II	A(c)	106.2	B	300	2	727	22.2 ± 0.9
	III	A(c)	98.4	B	300	3	721	22.0 ± 0.8
	IV		91.8	B	300	1	1597	21.4
1.5% Pt/TiO ₂ (HTR)	I	64.5	C	320	5	105.4	23.4 ± 5.0	
			C	215	5	46.0	9.2 ± 2.5	
2.0% Pt/TiO ₂ (HTR)	I	A(c)	108.6	C	300	2	24.7	10.3 ± 3.6
	II	A(c)	106.2	C	300	2	58.7	23.5 ± 5.0
	III	A(c)	98.4	C	300	3	39.8	15.9 ± 3.9

(a) After correction for irreversible adsorption on the support

(c) A Indicated values obtained after treatment in 20% O₂/80% He at 673K for 30 min followed by an LTR or HTR step.

(W) Water-treated catalyst.

* Pretreatment B except that T_{Red} = 175°C

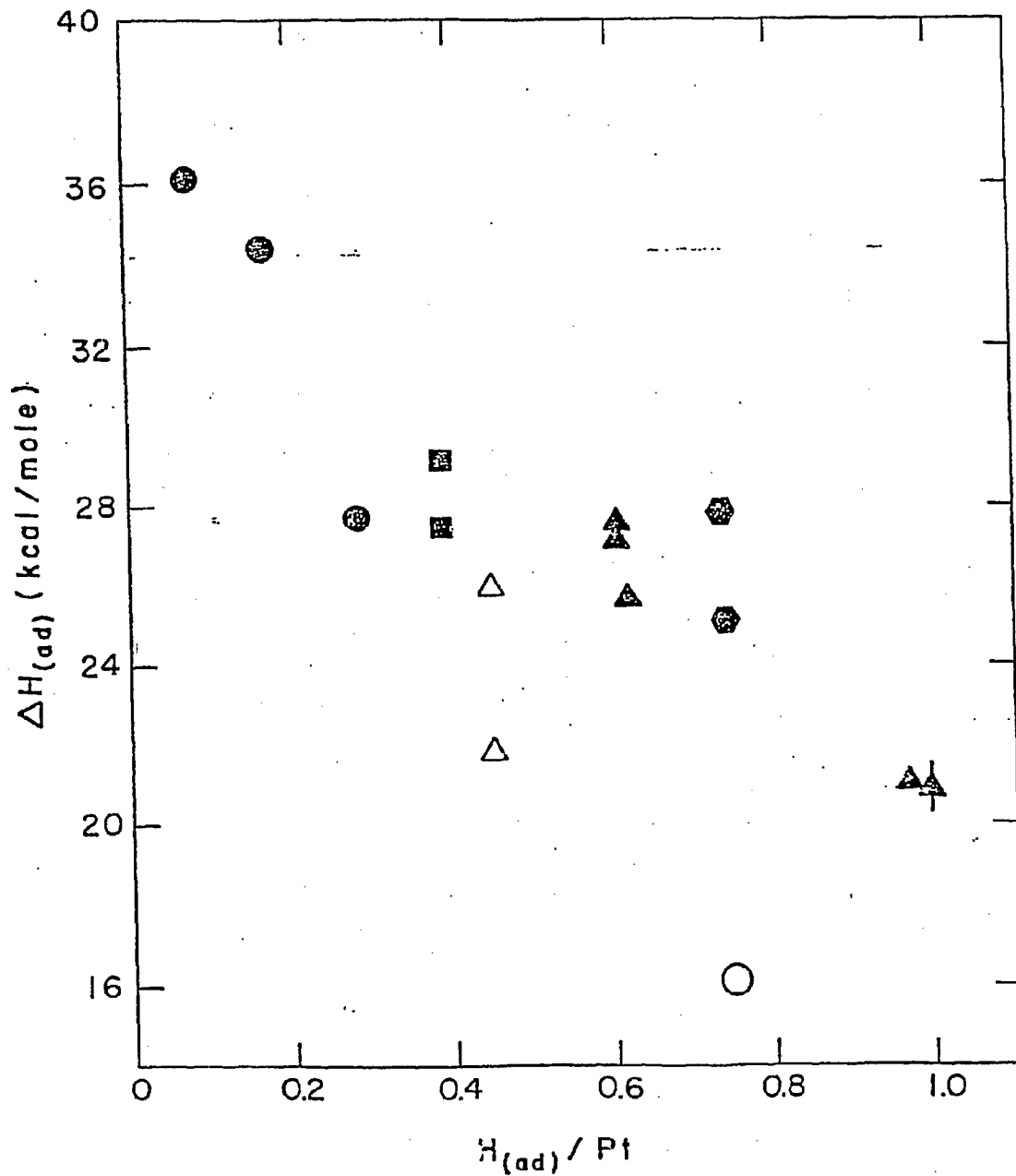
** 16 hr reduction at 175°C

TABLE 3

INTEGRAL HEATS OF ADSORPTION ON SUPPORTED PALLADIUM (300K)

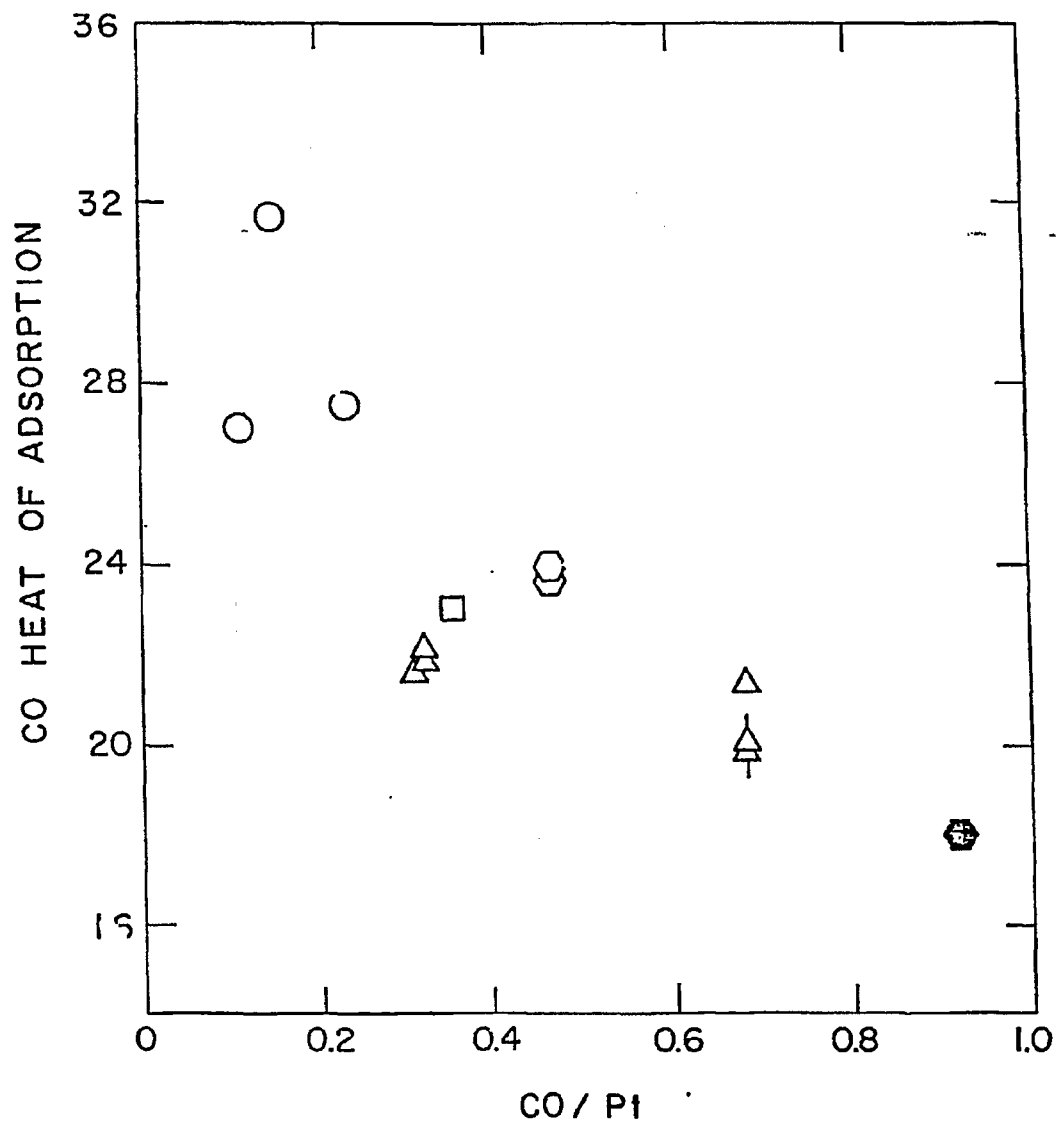
Catalyst	T _{Red} (°K)	Dia- meter (nm)	ΔH _(ad)		
			H ₂	O ₂	CO
2.1% Pd/SiO ₂	573	1.7	32	70	29
0.48% Pd/SiO ₂	573	2.4	35	60	30
1.95% Pd/SiO ₂ -Al ₂ O ₃	448	3.2	32	55	22
1.95% Pd/SiO ₂ -Al ₂ O ₃	673	4.0	33	50	22
1.80% Pd/η-Al ₂ O ₃	673	3.4	31	61	20
2.03% Pd/TiO ₂	448	3.7	33	71	--
2.03% Pd/TiO ₂ (O ₂ @573K)	448	3.6	32	62	24
2.03% Pd/TiO ₂	773	(3.7)	26	--	17

FIGURE 1



Correlation of H_2 Heat of Adsorption with Pt Dispersion: 2.1% Pt/SiO₂ - ●, 1.5% Pt/SiO₂-Al₂O₃ - ■, 2.1% Pt/ η -Al₂O₃ - ⬠, 2.0% Pt/TiO₂ (LTR) - ▲, 2.0% Pt/TiO₂ (LTR) after O₂ exposure and rereduction - △, 1.5% Pt/TiO₂ (LTR) - ▲, Pt/SiO₂ (from Reference 20) - ○.

FIGURE 2



Variation of CO $\Delta H_{(ad)}$ with CO/Pt (i.e., Pt Crystallite Size):
 2.1% Pt/SiO₂ - ○ , 1.5% Pt/S-A - □ , 2.1% Pt/ η -Al₂O₃ - ○ ,
 2.0% Pt/TiO₂ (LTR) - △ , 1.5% Pt/TiO₂ (LTR) - △ , 1% Pt/Al₂O₃ - ● .
 (from Ref. 3).

FIGURE 3

HEAT OF ADSORPTION OF CO ON
SUPPORTED PALLADIUM (300K)

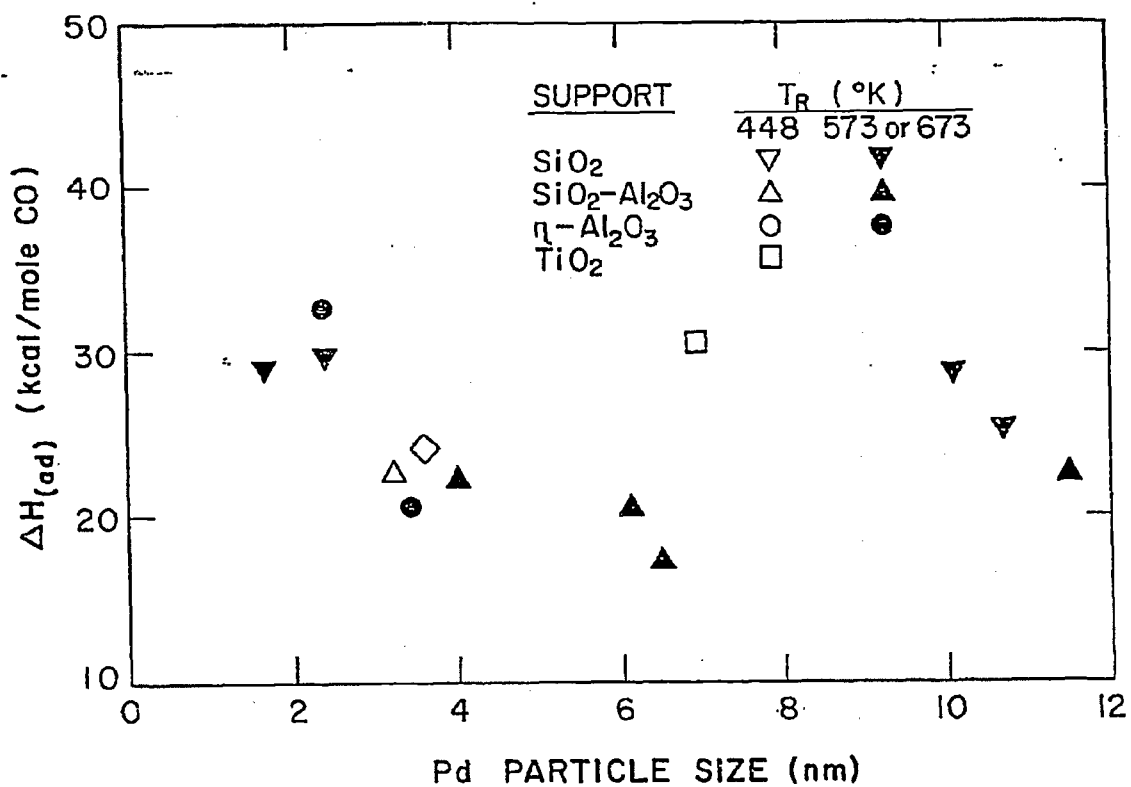


FIGURE 4
 HEAT OF ADSORPTION OF O₂ ON
 SUPPORTED PALLADIUM (300K)

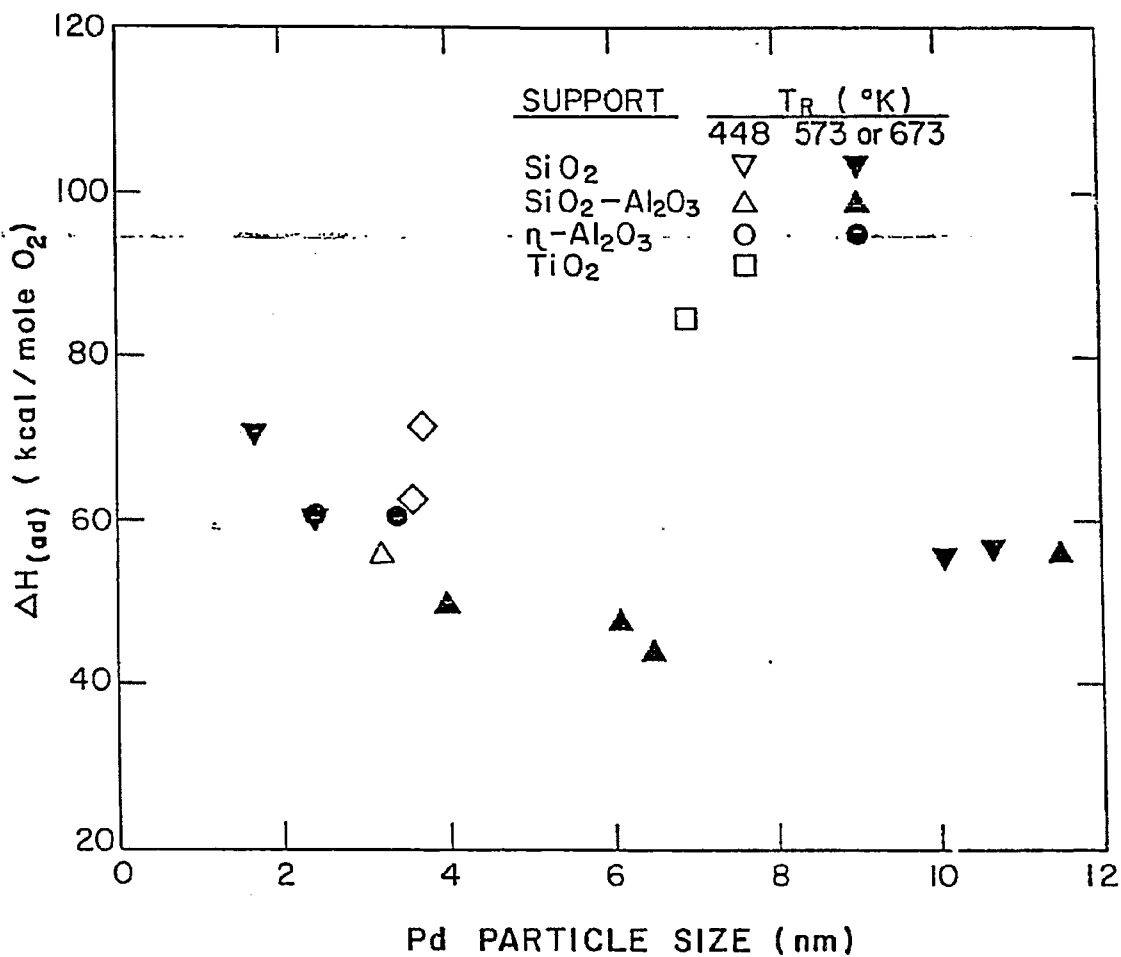


FIGURE 5

HEAT OF ADSORPTION OF H₂ ON
SUPPORTED PALLADIUM (300K)

