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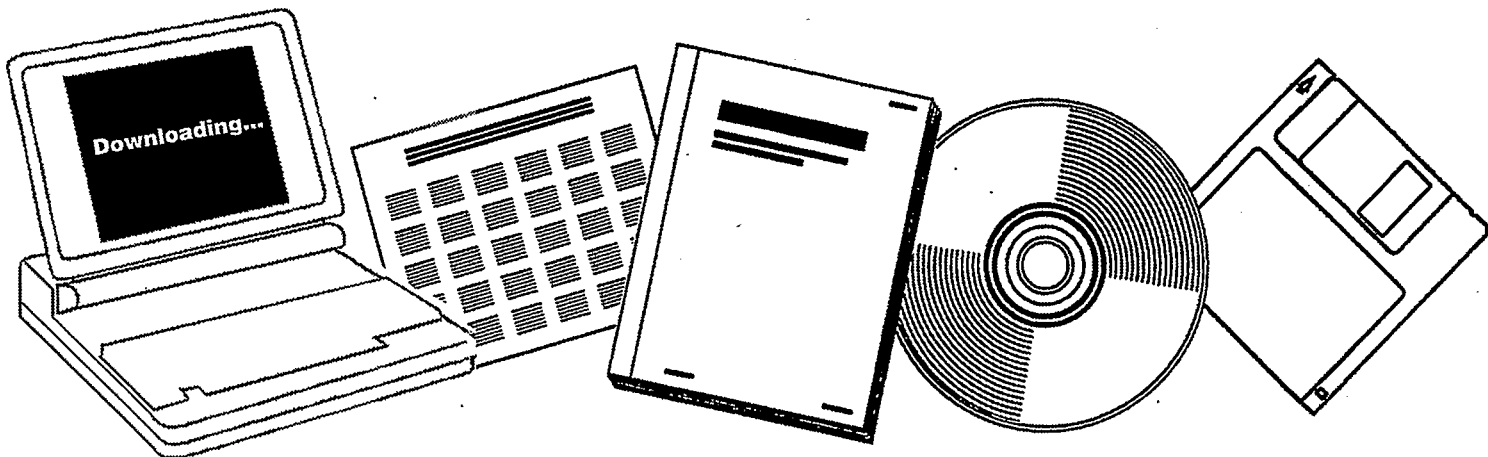
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**CHARACTERIZATION OF CATALYSTS WITH  
METAL-SUPPORT EFFECTS AND OF THE SPECIES  
ADSORBED ON THEIR SURFACES: FINAL PROGRESS  
REPORT, SEPTEMBER 1, 1984--AUGUST 30, 1988**

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

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

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## Research Summary

The principal objectives of our current grant were: "to gain a better understanding of the chemistry and physics which produce these metal-support effects and, as a consequence, to use this information to guide us in the development of new and improved catalyst systems for particular reactions." We chose to do this by investigating Pt and Pd dispersed on selected supports using a multifaceted approach involving DSC, TGA, NMR, adsorption, and kinetic studies of selected probe reactions. This approach has proven to be very fruitful as it has led us to the preparation of: 1) the most active Pd catalysts to date for benzene hydrogenation; 2) the most active Pt catalysts to date (by more than an order of magnitude) for acetone hydrogenation to isopropanol; and 3) the only Pt catalysts capable of significant selectivity to crotyl alcohol during crotonaldehyde hydrogenation. In addition, our calorimetric studies using DSC have shown that the principal reason for decreased chemisorption capacity on TiO<sub>2</sub>-supported Pt and Pd is the physical blockage of metal surface by TiO<sub>x</sub> species rather than by a large decrease in the heats of adsorption, Q<sub>ad</sub>. Also, with Pd a large crystallite size effect was found which increased Q<sub>ad</sub> values on particles smaller than 3 nm. Each of these aspects will be addressed separately in the following discussion, and the references pertain to those listed under Publications.

### Q<sub>ad</sub> Measurements on Pt

In this study Pt was dispersed on SiO<sub>2</sub>,  $\eta$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> and both chemisorption and DSC measurements were made to examine the influence of metal-support effects on heats of adsorption. Isothermal, integral Q<sub>ad</sub> values for H<sub>2</sub> were somewhat, but not markedly, lower on TiO<sub>2</sub>-supported Pt giving values around 12-13 kcal/mole H<sub>2</sub> compared to about 14 kcal/mole H<sub>2</sub> on typical catalysts, the latter of which is in good agreement with UHV results (2,3,6).

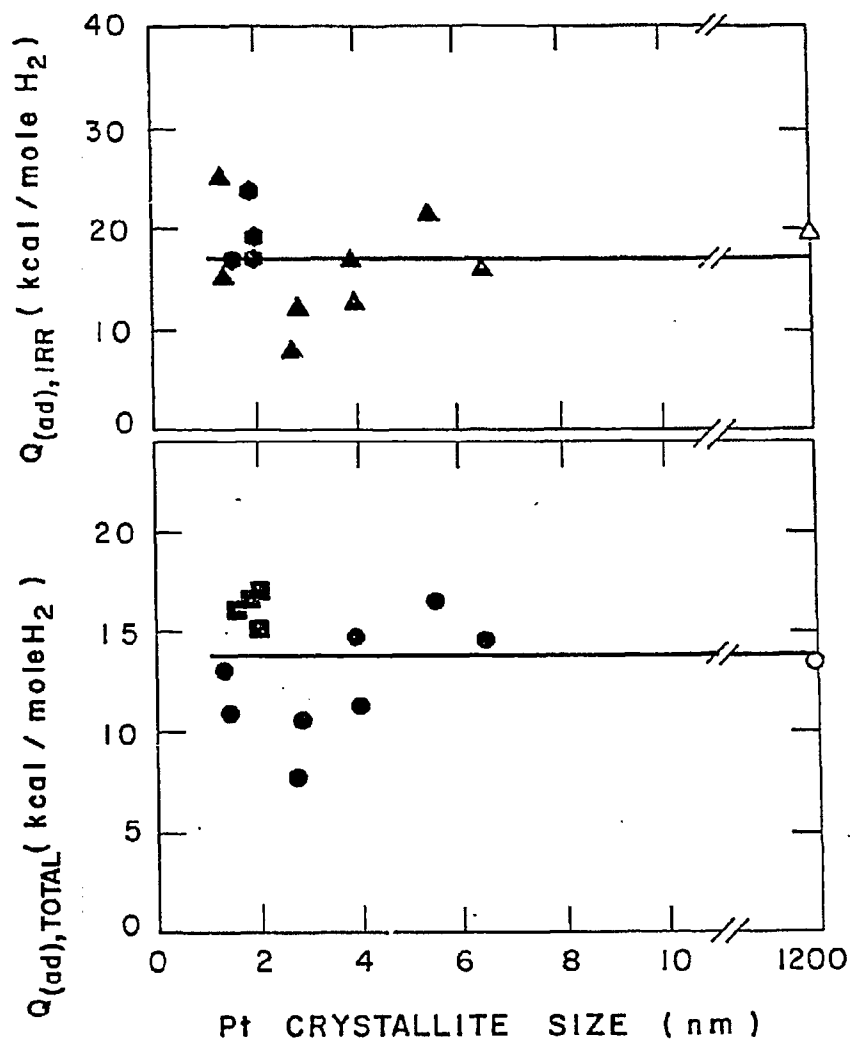
An artifact was found due to changes in the gas phase thermal conductivity, which was previously unrecognized with the operation of this type of calorimeter, but techniques were found to eliminate this problem, which was most pronounced with H<sub>2</sub> (6,7). The Q<sub>ad</sub> values for CO on these catalysts varied from 32 kcal/mole on Pt/SiO<sub>2</sub> samples to 21 kcal/mole on Pt/TiO<sub>2</sub> samples after a high temperature reduction (HTR). This was the only significant apparent support effect observed in this study, and it resulted in the intriguing activity correlation shown in Reference 4. Platinum clearly showed no crystallite size effect down to 1 nm particles, as indicated in Figure 1.

#### Q<sub>ad</sub> Measurements on Pd

The behavior of Pd on these same supports was decidedly different than that of Pt (1,5). There was no significant influence of the support on heats of adsorption, and Q<sub>ad</sub> values at 300K of 15 ± 1 kcal/mole H<sub>2</sub>, 23 ± 3 kcal/mole CO, and 50 ± 6 kcal/mole O<sub>2</sub> were obtained on crystallites between 3 and 1000 nm (8-10). Perhaps the most striking finding of this investigation was a significant rise in Q<sub>ad</sub> values, which increased up to 60% for all three gases on the smallest particles, as crystallite size decreased below 3 nm (8-10). An example of this trend is exhibited by Figure 2. These highest values are close to initial Q<sub>ad</sub> values reported in the UHV literature for each gas. Although we believe the cause is primarily due to a change in the electronic properties of the Pd particles, the more open faces on the small crystallites could reduce interactions between surface molecules or atoms thereby approximating the lower surface coverage state on single crystals.

#### Benzene Hydrogenation over Pd

This reaction represents the initial model compound in our study of the hydrogenation of aromatic hydrocarbons to obtain kinetic information related to upgrading coal liquids. We found, as others have, that the support chosen



Integral heats of adsorption of H<sub>2</sub> on silica-supported Pt as a function of crystallite size (P<sub>H<sub>2</sub></sub> = 10 KPa, T = 300 K):  
 ●, ▲ - Pt/SiO<sub>2</sub> prepared from inorganic precursor; ■, ● - Pt/SiO<sub>2</sub> prepared from organometallic precursor; ○, △ - Pt powder.

Figure 1

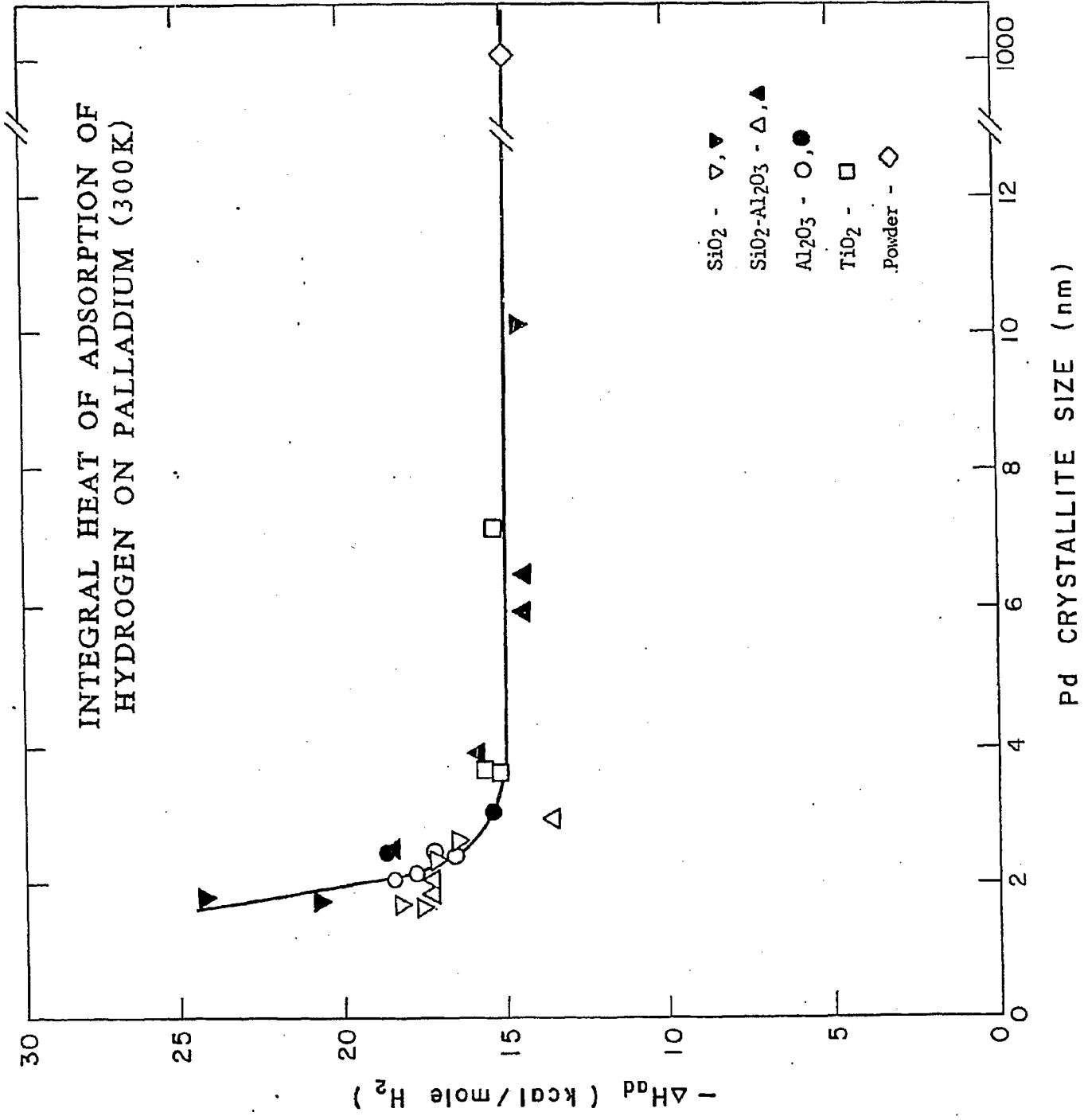
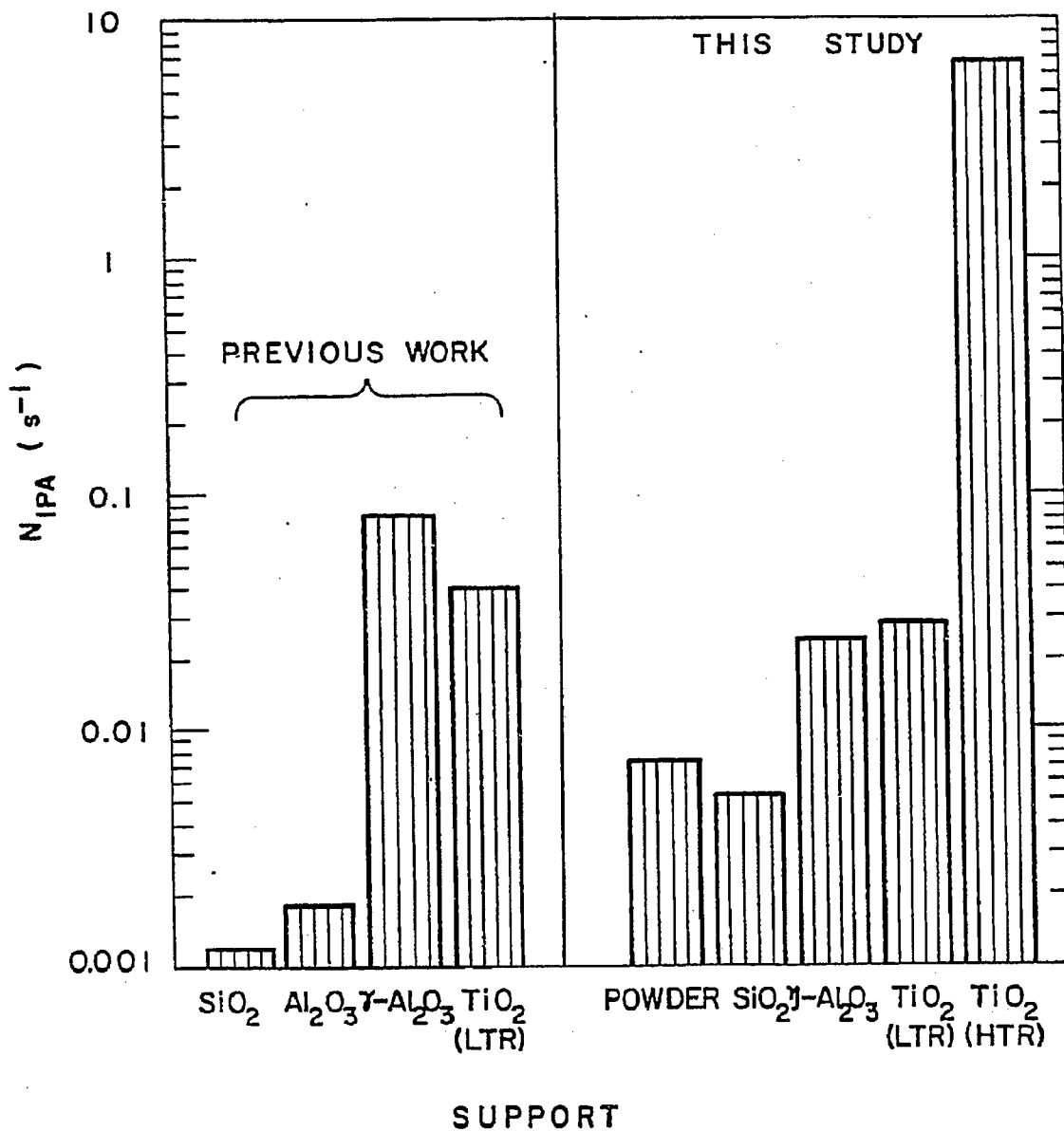


Figure 2

can noticeably increase specific activity; however, we were able to prepare catalysts using acidic supports that were 10 times better than typical Pd catalysts and four times more active than the previous most active catalysts (11). This was attributed to an increase in adsorption sites for benzene in the Pd-support interface region. A detailed, modified Langmuir-Hinshelwood kinetic model, which proposed and incorporated partially dehydrogenated benzene species on the Pd surface, was able to explain the kinetic behavior of all catalysts studied (12). The unique inclusion of these hydrogen-deficient benzene species not only explained the high reaction orders in  $H_2$ , but also resolved conflicts in the literature related to isotopic exchange and deactivation reactions involving benzene (12).

#### Hydrogenation of Carbonyl Bonds

We have previously proposed a model to explain the much higher CO hydrogenation rates obtained over  $TiO_2$ -supported Pt [Vannice and Sudhakar, J. Phys. Chem. 88, 2429 (1984)]. It states that special sites are created at the Pt-support interface as a consequence of oxygen removal from the titania, and these sites can interact with the oxygen end of the CO molecule to facilitate bond rupture. We decided to test this hypothesis further to see if other carbonyl bonds could be activated in a similar fashion, and our first probe reaction was acetone hydrogenation. The results were almost identical to those observed for CO hydrogenation: 1) Turnover frequencies over (HTR) Pt/ $TiO_2$  were increased up to 1000-fold over typical (Pt/ $SiO_2$ ) catalysts (as shown in Figure 3); 2) partial pressure dependencies were similar on all catalysts; and 3) activation energies were similar on all catalysts (13). Again, the rate increase is associated with the preexponential factor implying, most likely, a large increase in active site concentration (14).



Comparison of turnover frequency for the formation of isopropanol from acetone at 303 K, as a function of the support ( $P = 1$  atm,  $H_2/AC = 3.06$ ).

Figure 3



Additional studies with different Pt crystallite sizes and Pt-Au alloys showed isopropanol formation to be a structure-insensitive reaction.

This verification of our model led us to change our direction of research somewhat and to test the model even more rigorously by hypothesizing that these sites could selectively activate carbonyl bonds in a molecule also containing multiple C=C bonds. Our probe reaction was crotonaldehyde ( $\text{CH}_3\text{-CH=CH-CHO}$ ) hydrogenation to determine if crotyl alcohol, rather than butyraldehyde, could be favored by such metal-support interactions. This would be a demanding test because Pt is known in the literature to give 100% butyraldehyde, and our results with Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts confirmed this. However, selectivities to crotyl alcohol from 13 to 37% were obtained with Pt/TiO<sub>2</sub>, and the highest values obtained were with the HTR catalysts, as shown in Figure 4 (15). These encouraging results again provide support for our explanation -- the creation of new interfacial sites that selectively activate C=O bonds. This potential for selective hydrogenation, which is stated in our current grant proposal, will be tested further in our future studies by choosing aromatic and olefinic hydrocarbon molecules also containing carbonyl bonds.

#### Solid-State NMR of Pt Catalysts

This portion of our program, which is focused on <sup>13</sup>C O adsorption on Pt and Knight shift studies of <sup>195</sup>Pt, has been delayed for several reasons. First, our NSF equipment grant was not awarded the first year it was submitted. Second, delivery of the 300 MHz system was delayed, and the system became operational only this fall. Finally, the individual selected for the postdoctoral position has taken longer to complete his thesis than anticipated, and he will now arrive in February, 1988. This effort remains as an integral part of our study and our original interests and objectives --

# EFFECT OF HTR PRETREATMENT ON Pt/TiO<sub>2</sub> CATALYSTS

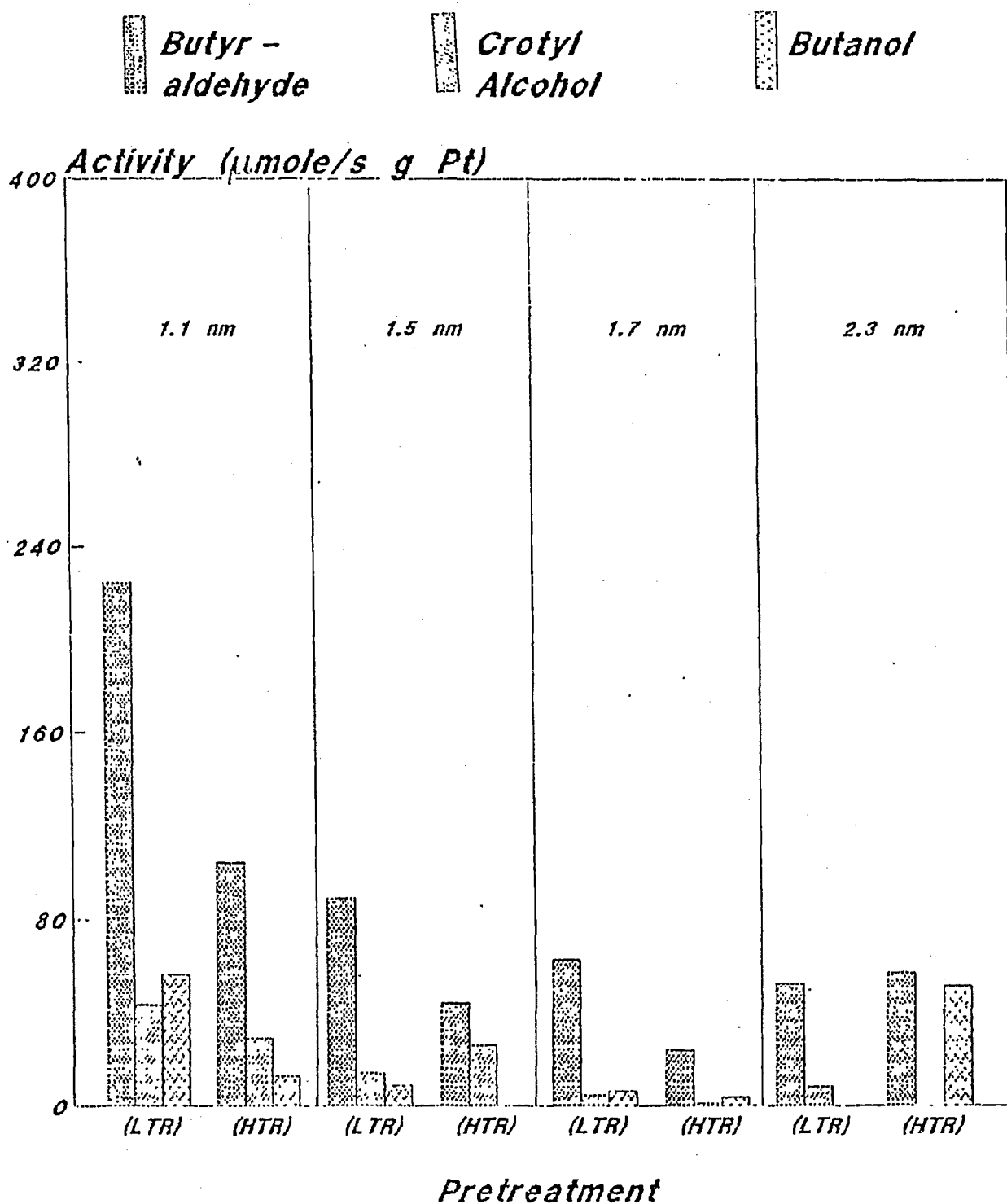


Figure 4

identifying different forms of C on Pt catalysts and characterizing electronic properties of Pt crystallites dispersed on different supports -- remain intact.

### Personnel

During this period of time two PhD students, Pen Chou and Bishwajit Sen, and one M.S. student, Tom Leong, completed their theses. Dr. Chou is working at Union Carbide and Dr. Sen is a postdoctoral fellow in Professor John Falconer's lab at the University of Colorado. A new student began work on his M.S. degree this past fall, and a postdoctoral offer to Dr. Dan Barabino, from Professor Cecil Dybowski's group at the University of Delaware, was accepted. He will join our group on February 1, 1988, to participate in the solid-state MAS-NMR portion of this program.

### Publications

During the past three years, 12 publications have appeared describing our DOE-sponsored work and reprints of the five most recent are attached. Two manuscripts have been submitted and two are in their final stages of preparation. These publications are:

1. Vannice, M. A. and Chou, P., "Heats of Adsorption of H<sub>2</sub> and CO on a Pd/TiO<sub>2</sub> "SMSI" Catalyst," JCS Chem. Comm., (1984), 1590.
2. Vannice, M. A., Hasselbring, L. C., and Sen, B., "Metal-Support Effects on H<sub>2</sub> and CO Heats of Adsorption on TiO<sub>2</sub>-Supported Pt," J. Phys. Chem., 89, 2972 (1985).
3. Vannice, M. A., Hasselbring, L. C., and Sen, B., "Direct Measurements of Heats of Adsorption on Pt Catalysts. I. H<sub>2</sub> on Pt Dispersed on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>," J. Catal., 95, 57 (1985).
4. Vannice, M. A., Hasselbring, L. C., and Sen, B., "Ibid. II. CO on Pt Dispersed on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>," J. Catal., 97, 66 (1986).
5. Vannice, M. A. and Chou, P., "CO, O<sub>2</sub> and H<sub>2</sub> Heats of Adsorption on Supported Palladium", ACS Symposium Series, 298, 76 (1986).

6. Sen, B., Chou, P., and Vannice, M. A., "Direct Measurements of Heats of Adsorption on Pt Catalysts. III. Potential Errors with Differential Scanning Calorimeters," J. Catal. 101, 517 (1986).
7. Vannice, M. A., Sen, B., and Chou, P., "Modifications Required to a Power-Compensated DSC to Obtain Accurate Heat of Adsorption Measurements," Rev. Sci. Instru., 58, 647 (1987).
8. Chou, P. and Vannice, M. A., "Calorimetric Heat of Adsorption Measurements on Palladium. I. Influence of Crystallite Size and Support on Hydrogen Adsorption," J. Catal., 104, 1 (1987).
9. Chou, P. and Vannice, M. A., "Ibid. II. Influence of Crystallite Size and Support on CO Adsorption," J. Catal., 104, 17 (1987).
10. Chou, P. and Vannice, M. A., "Calorimetric Heat of Adsorption Measurements on Palladium. III. Influence of Crystallite Size and Support on O<sub>2</sub> Adsorption," J. Catal. 105, 342 (1987).
11. Chou, P. and Vannice, M. A., "Benzene Hydrogenation over Supported and Unsupported Pd. I. Kinetic Behavior," J. Catal. 107, 129 (1987).
12. Chou, P. and Vannice, M. A., "Ibid. II. Reaction Model, J. Catal. 107, 140 (1987).
13. Sen, B. and Vannice, M. A., "Acetone Hydrogenation over Pt Catalysts." J. Catal., In Press.
14. Sen, B. and Vannice, M. A., "Metal-Support Effects on Crotonaldehyde Hydrogenation," In Press.
15. Sen, B. and Vannice, M. A., "Heats of Adsorption of H<sub>2</sub>, CO, and O<sub>2</sub> on SiO<sub>2</sub>-Supported Pt," In Prep.

#### Presentations

This work has been presented and discussed at 14 regional and national meetings and at 12 universities and research laboratories.

#### Budget Statement

All funds will have been expended by the end of this grant except those encumbered for the remainder of Dr. Barabino's stay.