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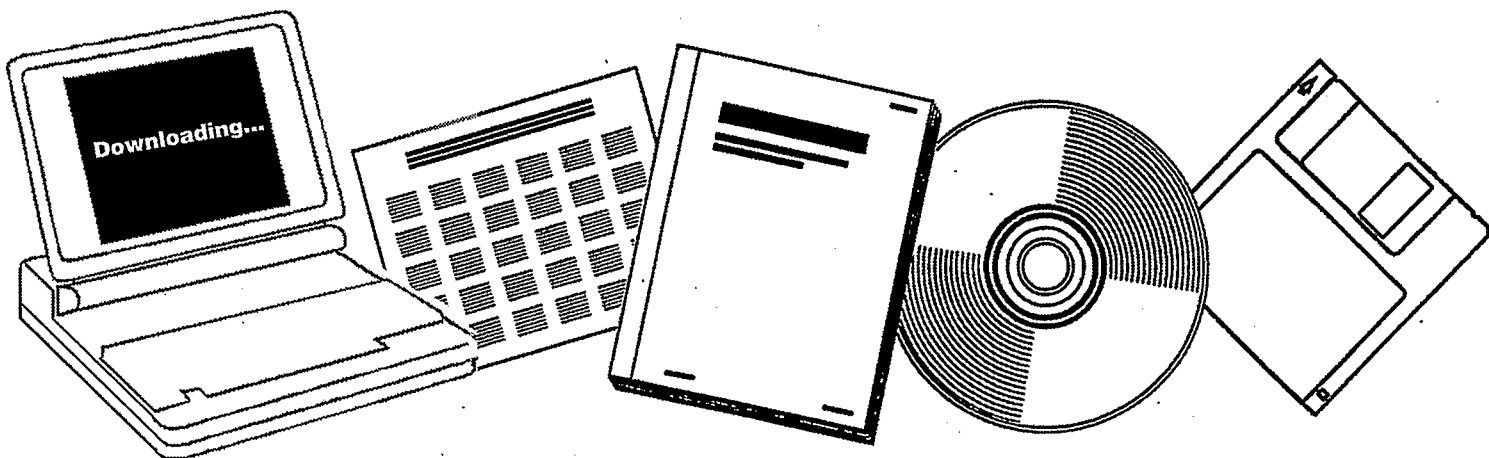
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**CHARACTERIZATION OF CATALYSTS WITH  
METAL-SUPPORT EFFECTS AND OF THE SPECIES  
ADSORBED ON THEIR SURFACES: PROGRESS  
REPORT, SEPTEMBER 1, 1986-AUGUST 30, 1987**

**PENNSYLVANIA STATE UNIV., UNIVERSITY  
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CHARACTERIZATION OF CATALYSTS WITH METAL-SUPPORT  
EFFECTS AND OF THE SPECIES ADSORBED ON THEIR SURFACES

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May 28, 1987

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### Research Summary

During the past year we have continued our investigation of Pt crystallite size effects on  $\Delta H_{ad}$  by varying particle sizes from 1.5 to 1500 nm on  $SiO_2$ . This property for CO and  $H_2$  adsorption on Pt is much less affected by crystallite size than on Pd, as shown in Figure 1. We have completed our study of heats of adsorption on Pd and this work has appeared in three recent papers in the Journal of Catalysis (3-5). It also has provided insight into the  $H_2$ - $D_2$  exchange reaction on Pd (8).

We have completed our study of  $C_6H_6$  hydrogenation over Pd catalysts and have proposed a unique universal model that incorporates deposition of dehydrogenated benzene species under reaction conditions. This work will appear soon in the Journal of Catalysis (6,7).

We have found that the rate of acetone hydrogenation to isopropanol can be enhanced 100- to 1000-fold over  $TiO_2$ -supported Pt, as shown in Figure 2. This result is very similar to that for CO hydrogenation and it provides strong support for our premise that carbonyl bonds in an organic molecule may be activated in a manner similar to that found previously for the CO molecule thereby giving improved hydrogenation catalysts. Our ongoing studies of crotonaldehyde ( $CH_3-CH=CH-CHO$ ) hydrogenation have provided evidence that selective hydrogenation of the C=O bond compared to the C=C bond can be induced by a metal-support effect. As shown in Figure 3, only butyraldehyde is obtained over Pt on typical supports like  $SiO_2$  and  $Al_2O_3$  whereas the use of  $TiO_2$  can produce over 35% crotyl alcohol, depending on the pretreatment. These are very encouraging results.

Our TGA system is now working, and we have completed construction of our mobile mass spectrometer analytical system. It is now operational.

### Personnel

One PhD student, Pen Chou, graduated in December and he is now working at Union Carbide. Another student will be completing his PhD thesis this summer. We have been searching for a postdoctoral fellow with a strong background in solid-state MAS-NMR, but without success so far. However, I am aware of some students with this expertise who are near graduation, and I am hopeful that one will join our group. One new student will be added to this project this fall.

### Publications

During the past year, four publications have appeared describing our DOE-sponsored work and copies are attached. Four manuscripts are in press and two are in their final stages of preparation. These publications are:

1. Sen, B., Chou, P., and Vannice, M. A., "Direct Measurement of Heats of Adsorption on Pt Catalysts. III. Potential Errors with Differential Scanning Calorimeters;" J. Catal., 101, 517 (1986).
2. Vannice, M. A., Sen, B., and Chou, P., "Modifications Required to a Power-Compensated DSC to Obtain Heat of Adsorption Measurements," Rev. Sci. Instru., 58, 647 (1987).
3. 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).
4. Chou, P. and Vannice, M. A., "Ibid. II. Influence of Crystallite Size and Support on CO Adsorption," J. Catal., 104, 17 (1987).
5. Chou, P. and Vannice, M. A., "Calorimetric Heats of Adsorption Measurements on Palladium. III. Influence of Crystallite Size and Support on O<sub>2</sub> Adsorption," J. Catal. In Press.
6. Chou, P. and Vannice, M. A., "Benzene Hydrogenation over Supported and Unsupported Pd. I. Kinetic Behavior," J. Catal. In Press.
7. Chou, P. and Vannice, M. A., "Ibid. II. Reaction Model," J. Catal. In Press.
8. Vannice, M. A., "The H<sub>2</sub>-D<sub>2</sub> Exchange Reaction on Pd," J. Catal., Accept. for Pub.
9. Sen, B. and Vannice, M. A., "Acetone Hydrogenation over Pt," To be Submitted.

10. Sen, E. and Vannice, M. A., "Crotonaldehyde Hydrogenation over Pt Catalysts," To be Submitted.

FIGURE 1

INTEGRAL HEATS OF ADSORPTION ON  
SiO<sub>2</sub>-SUPPORTED Pt ( 300 K )

▲ Hydrogen

● Carbon  
Monoxide

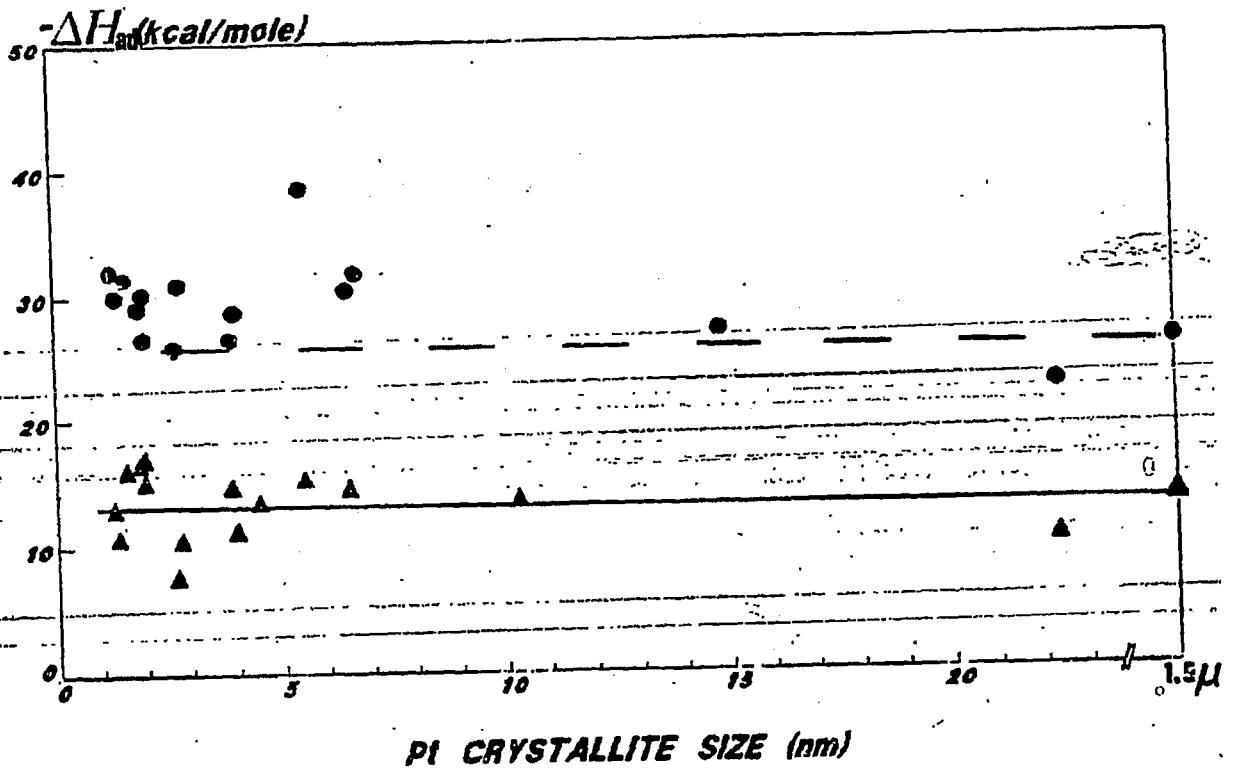


FIGURE 2

ACETONE TOF MARKEDLY INCREASED  
OVER HTR Pt/TiO2 CATALYST

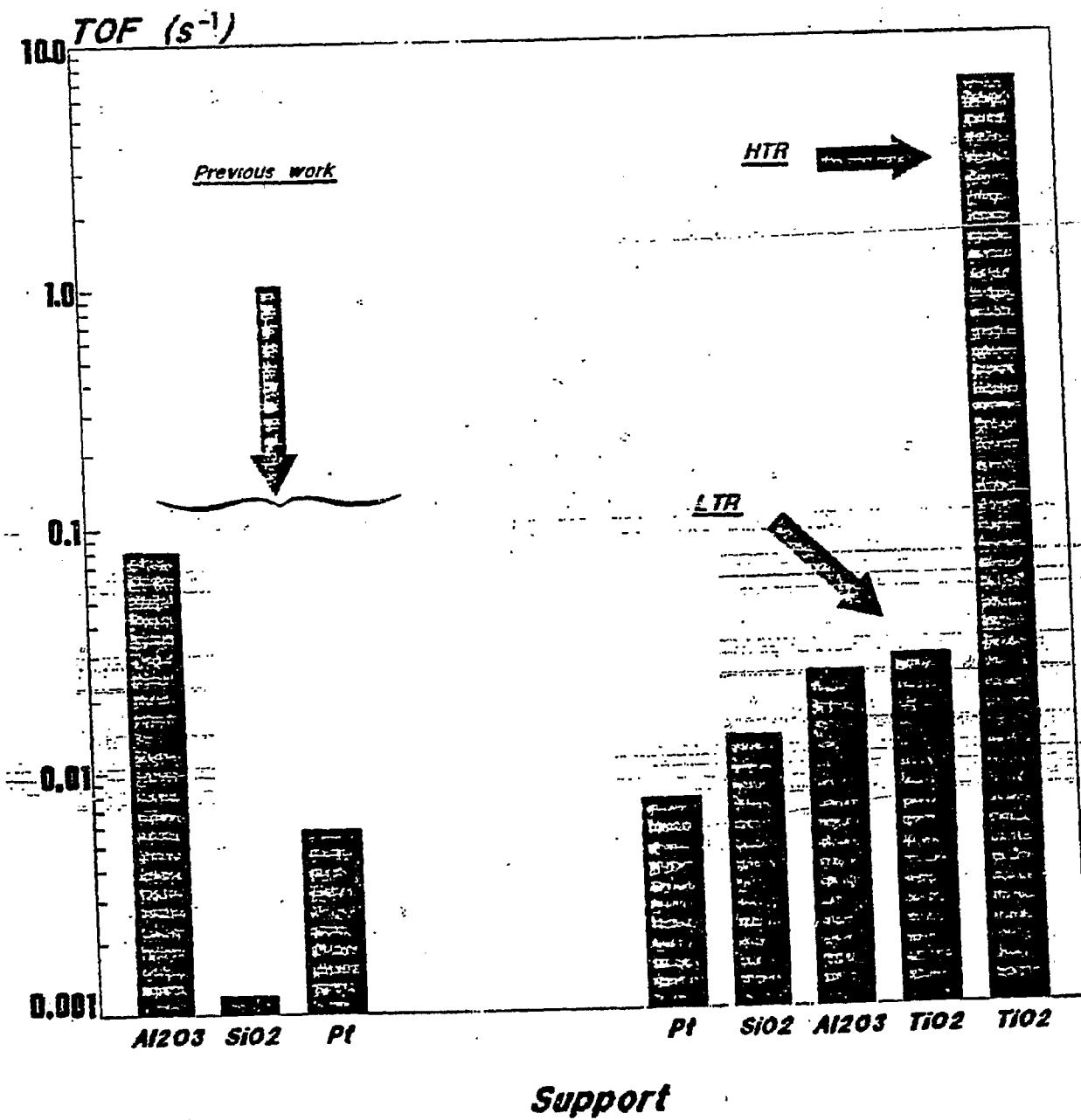


FIGURE 3

ONLY TiO<sub>2</sub>-SUPPORTED CATALYSTS  
EXHIBITED ANY SELECTIVITY TO CROTYL  
ALCOHOL

Butyr-  
aldehyde

Crotyl-  
Alcohol

Butanol

