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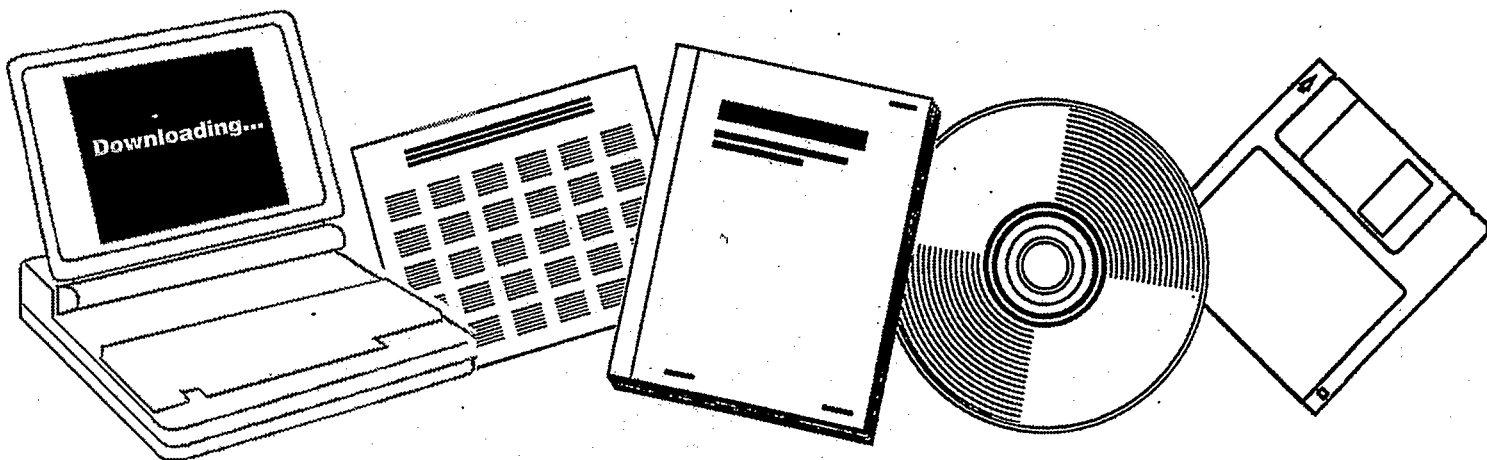
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## ENHANCEMENT OF ACTIVITY AND SELECTIVITY BY METAL-SUPPORT INTERACTIONS (MSI). PROGRESS REPORT, SEPTEMBER 1, 1988--JUNE 30, 1991

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**ENHANCEMENT OF ACTIVITY AND SELECTIVITY  
BY METAL-SUPPORT INTERACTIONS (MSI)**

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## Research Summary

### A. Toluene and Xylene Hydrogenation over Pd

During this period, we completed the study related to support effects on the hydrogenation kinetics of toluene and ortho-, meta-, and para-xylene over a family of Pd catalysts. Behavior among different catalysts for each reaction was similar to that of benzene, but the relative enhancements over a given catalyst decreased in the order: benzene > toluene > p-xylene > m-xylene > o-xylene. Equilibrium adsorption constants for the aromatic compounds obtained from computer fitting the rate equations increased in the opposite order. The model originally proposed for benzene appears applicable to these other aromatics — acid sites on the support near the Pd particles provide additional active sites for the adsorption of the aromatic and its subsequent hydrogenation via H spillover from the Pd surface. One of the most important findings of this study was that the apparent turnover frequency could be enhanced by the appropriate choice of an acidic support, with such increases ranging from 27 for benzene to over 2 for m-xylene, as shown in Table 1. Further details are provided in the two publications in the Journal of Catalysis describing this work (#4 and #5 in the Publications section).

### B. Benzene and Toluene Hydrogenation over Pt

After obtaining these enhanced activities with Pd, we wished to determine if the same behavior existed with Pt, so Pt was dispersed on the same  $\text{SiO}_2$ ,  $\eta\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$  and  $\text{TiO}_2$  supports and both benzene and toluene hydrogenation was studied. The principal results are given in Tables 2-4 and can be summarized as follows.

First, turnover frequencies (TOF's) are typically 50-100 times higher on Pt than on Pd (see our publication #4), but the activation energies for each reaction are very similar and nearly identical to those obtained with Pd, i.e., the average values for benzene and toluene hydrogenation on supported Pt were 11.8 and 11.9 kcal/mole, respectively, versus 12.0 and 11.8 for these two reactions

TABLE 1

Contribution of Interfacial Acid Sites to  
Hydrogenation of Aromatic Hydrocarbons Relative to Sites on Pd

Hydrocarbon	$r_I/r_{Pd}^a$	
	Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Pd/TiO <sub>2</sub>
Benzene	27.0	12.0
Toluene	6.8	6.4
o-Xylene	4.4	4.4
m-Xylene	2.3	2.3
p-Xylene	2.6	4.1
o-Xylene <sup>b</sup>	3.9	3.9

<sup>a</sup> $r_I/r_{Pd} = (TOF_{Total} - TOF_{Pd})/TOF_{Pd}$ , where  $TOF_{Pd}$  is the average on Pd powder, Pd/MgO, Pd/SiO<sub>2</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub> at 413 K, 680 Torr H<sub>2</sub> and 50 Torr aromatic.

<sup>b</sup>For isomerization reaction to m-xylene.

TABLE 2

Kinetics of Benzene Hydrogenation over Pt<sup>a)</sup>

Catalyst	Dispersion (H <sub>2d</sub> /Pt)	E <sub>act</sub> (kcal/mol)	Activity @ 60°C	
			μmol/s · g cat	TOF (s <sup>-1</sup> × 1000)
0.96% Pt/SiO <sub>2</sub> - I	0.96	11.4 ± 2.2	4.19	89
0.96% Pt/SiO <sub>2</sub> - II	0.96	11.0 ± 1.9	4.38	93
0.78% Pt/Al <sub>2</sub> O <sub>3</sub> - I	1.0	11.1 ± 2.1	0.62	15
0.78% Pt/Al <sub>2</sub> O <sub>3</sub> - II	1.0	11.8 ± 0.8	0.60	15
0.24% Pt/SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> - I	0.44	12.0 ± 1.4	0.30	55
0.24% Pt/SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> - II	0.44	10.1 ± 1.0	0.39	72
0.95% Pt/TiO <sub>2</sub> (LTR) - I	0.73	12.7 ± 0.4	2.66	75
0.95% Pt/TiO <sub>2</sub> (LTR) - II	0.73	12.6 ± 0.6	2.77	78
0.95% Pt/TiO <sub>2</sub> (HTR) - I	---	13.1 ± 1.1	1.81	--
0.95% Pt/TiO <sub>2</sub> (HTR) - II	---	12.1 ± 0.6	1.56	--
0.95% Pt/TiO <sub>2</sub> (HTR) - III	---	11.7 ± 1.1	2.97	--

<sup>a)</sup>P<sub>Bz</sub> = 50 torr and P<sub>H2</sub> = 680 torr

TABLE 3  
Kinetics of Benzene Hydrogenation over Pt<sup>a)</sup>

Catalyst	Dispersion (H <sub>2d</sub> /Pt)	E <sub>act</sub> (kcal/mol)	Activity @ 60°C	
			μmol/s · g cat	TOF (s <sup>-1</sup> × 1000)
0.96% Pt/SiO <sub>2</sub> - I	0.96	10.3 ± 1.5	4.94	105
0.96% Pt/SiO <sub>2</sub> - II	0.96	11.7 ± 1.7	6.09	129
0.78% Pt/Al <sub>2</sub> O <sub>3</sub> - I	1.0	11.4 ± 1.6	2.15	53
0.78% Pt/Al <sub>2</sub> O <sub>3</sub> - II	1.0	11.4 ± 1.7	2.06	51
0.24% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	0.44	13.0 ± 0.7	2.47	458
0.95% Pt/TiO <sub>2</sub> (LTR)	0.73	12.9 ± 1.3	8.57	243
0.95% Pt/TiO <sub>2</sub> (HTR)	---	12.4 ± 2.0	5.84	---
Pt Powder	0.001	7.0 ± 0.3	0.31	53

<sup>a)</sup>P<sub>Bz</sub> = 35 torr and P<sub>H<sub>2</sub></sub> = 700 torr

TABLE 4  
Kinetics of Toluene Hydrogenation over Pt<sup>a)</sup>

Catalyst	Dispersion (H <sub>ad</sub> /Pt)	E <sub>act</sub> (kcal/mol)	Activity @ 60°C	
			μmol/s · g cat	TOF (s <sup>-1</sup> × 1000)
0.96% Pt/SiO <sub>2</sub>	0.96	10.3 ± 1.0	1.27	27
0.78% Pt/Al <sub>2</sub> O <sub>3</sub> - I	1.0	12.2 ± 2.1	1.48	36
0.78% Pt/Al <sub>2</sub> O <sub>3</sub> - II	1.0	14.2 ± 1.5	0.95	23
0.24% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (175°C red.) - I	0.90	11.0 ± 1.1	0.58	52
0.24% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (175°C red.) - II	0.90	11.2 ± 2.1	0.56	51
0.24% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (400°C red.)	0.58	10.9 ± 2.1	0.59	82
0.24% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (450°C red.)	0.44	11.0 ± 1.4	0.60	112
0.95% Pt/TiO <sub>2</sub> (LTR)	0.73	12.9 ± 1.7	2.77	78
0.95% Pt/TiO <sub>2</sub> (HTR)	---	14.4 ± 3.1	1.34	---
0.09% Pt/TiO <sub>2</sub> (LTR) - I	0.80	13.9 ± 3.1	0.04	11
0.09% Pt/TiO <sub>2</sub> (LTR) - II	0.80	10.6 ± 4.2	0.05	14
0.09% Pt/TiO <sub>2</sub> (HTR)	—	10.3 ± 2.8	0.04	—

<sup>a)</sup>P<sub>Bz</sub> = 50 torr and P<sub>H<sub>2</sub></sub> = 680 torr

on Pd, respectively. Consequently, the preexponential factor exerts a major influence on relative activity.

Second, because of the higher intrinsic activity of the Pt, any contributions from the support are going to be less important and more difficult to detect. Indeed, at a benzene pressure of 50 torr, all catalysts had similar TOF's except for Pt/Al<sub>2</sub>O<sub>3</sub> (Table 2); however, at a lower benzene pressure of 35 torr the sequence of activity was similar to that observed for Pd — Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > Pt/TiO<sub>2</sub> > Pt/SiO<sub>2</sub> > Pt/Al<sub>2</sub>O<sub>3</sub> — and the TOF's were higher on all catalysts (Table 3). This may reflect a greater adsorption capacity for hydrogen under reaction conditions. As for Pd, a reversible activity maximum with temperature was obtained (Figure 1) which can be associated with benzene desorption from the metal surface.

Third, the partial pressure dependencies for benzene hydrogenation on Pt are  $0.6 \pm 0.1$  for H<sub>2</sub> and  $0.1 \pm 0.1$  for benzene, and temperatures between 40 and 80°C have little effect on these parameters (Figure 2). Also, some evidence for deactivation by the formation of hydrogen-deficient surface species was observed.

Fourth, under identical conditions TOF values for toluene were very similar to those for benzene (Table 5), whereas the former were noticeably smaller than the latter on Pd. The activity sequence was the same as that found for Pd, i.e., Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > Pt/TiO<sub>2</sub> > Pt/SiO<sub>2</sub> > Pt/Al<sub>2</sub>O<sub>3</sub>.

Finally, for toluene hydrogenation, the partial pressure dependency increased from about 0.7 to around 1.1 as the temperature increased from 60° to 110°C; however, the pressure dependency on toluene was relatively constant at  $0.1 \pm 0.1$  over this temperature range (Figure 3). These studies are now being prepared for publication.

### C. Hydrogenation Reactions over Au

We have also examined a family of Au/SiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts to test the concept forwarded by Frost [Nature 334, 557 (1988)] that oxygen vacancies are created on the support by



TABLE 5

Relative Rates of Benzene and Toluene Hydrogenation on Pt

Catalyst	Dispersion ( $H_{10}/Pt$ )	$E_a$ (kcal/mol)		TOF ( $s^{-1} \times 10^3$ ) <sup>a</sup>				TOF <sub>T</sub> /TOF <sub>B</sub>	
		Benzene		Toluene		Benzene		Toluene	
		100°C	60°C	100°C	60°C	100°C	60°C	100°C	60°C
0.96% Pt/SiO <sub>2</sub>	0.96	11.0	10.3	553	93	142	27	0.26	0.29
0.78% Pt/Al <sub>2</sub> O <sub>3</sub>	1.00	11.8	14.2	102	15	231	23	2.26	1.53
0.24% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	0.44	10.1	11.0	370	72	663	112	1.79	1.56
0.95% Pt/TiO <sub>2</sub> (LTR)	0.73	12.6	12.9	601	78	633	78	1.05	1.00
0.95% Pt/TiO <sub>2</sub> (HTR)	---	13.1	14.4	1.59 <sup>b</sup>	0.19	1.45 <sup>b</sup>	0.14	0.91	0.74

<sup>a</sup>Data compared at  $P_{Bz} = P_{Tol} = 50$ ,  $P_{H_2} = 680$  torr.<sup>b</sup>Based on activity per gram of Pt.

electron transfer from the support to the dispersed metal crystallites, and these vacancies at the surface of the oxide support (i.e.,  $\text{TiO}_2$ ) are the active sites enhancing the rate of certain reactions. If this were the situation, gold would induce such sites in a manner similar to Pt because their work functions are similar. However, all these Au catalysts were completely inactive for CO, acetone, and ethylene hydrogenation. Therefore, our results clearly show that this is not an appropriate explanation for "SMSI" behavior with  $\text{TiO}_2$  and the metal must be associated with these active sites. This study also showed that oxygen adsorption was activated on both the  $\text{Au/SiO}_2$  and  $\text{Au/TiO}_2$  systems, as shown in Figures 4 and 5 in the paper accepted by Catalysis Letters, which discusses these results in greater detail.

#### D. CO Oxidation over Au

The inactivity of the  $\text{Au/TiO}_2$  catalysts, in particular, for any of the three hydrogenation reactions made us consider the possibility that the Au surface may have been completely covered by  $\text{TiO}_x$  species, and we wished to verify that these catalysts indeed had accessible Au surface area by establishing their activity for some reaction. We chose to study CO oxidation not only because of our previous work in this area [Choi and Vannice, *J. Catal.* **127**, 465, 489 (1991)], but also because of the recent reports that  $\text{Au/Fe}_2\text{O}_3$  and  $\text{Au/MnO}_x$  systems possessed high activity at room temperature [Haruta et al., *J. Catal.* **115**, 301 (1989); Hoflund and coworkers, *J. Catal.* **129**, 114 (1991)]. As shown in Figure 4, gold does have substantial activity at temperatures near  $25^\circ\text{C}$ , as demonstrated by the  $\text{Au/SiO}_2$  catalyst, but the activation energy is very low. The activity of a 2.19%  $\text{Pd/Al}_2\text{O}_3$  catalyst is also shown for comparison. The  $\text{Au/TiO}_2$  (HTR) catalyst, which had a high temperature reduction (HTR) at 773K, was extremely active whereas the  $\text{Au/TiO}_2$  (LTR) sample, which had a low temperature reduction (LTR) at 473K, was quite inactive. However, a calcination step in oxygen at 673K after the HTR step followed by a LTR step produced the most active catalyst of all, as shown in Figure 5. This figure also shows a second run with another  $\text{Au/TiO}_2$  (HTR)

sample during which the  $O_2$  was slowly introduced to prevent a rapid increase in concentration. This produced a more active catalyst than that shown in Figure 4, but it still deactivated if temperatures were increased above  $125^\circ C$ . The activity per g Au of these latter two catalysts is up to three times higher than the most active Au catalyst previously reported under comparable conditions, as shown in Table 6. In addition, activity maintenance was very reasonable, as shown in Figure 6, and it appeared to be lining out with about 40-50% of its original activity after 24 h on stream. Consequently, this system could have applicability to NASA's problem of  $CO + O_2$  recombination in their  $CO_2$  lasers which orbit the earth and monitor weather conditions. In addition, maintenance of activity in the presence of water vapor would verify applications related to CO detection and air purification in energy-efficient (well insulated) offices and homes. Further studies on this system are required.

#### E. Hydrogenation of Acetophenone over Pt

One aspect of this current program was to examine the influence of MSI on intramolecular selectivity in hydrogenation reactions involving a carbonyl group and unsaturated  $C=C$  bonds, and acetophenone ( $C_6H_5COCH_3$ ) was one of our probe molecules to study the rate of hydrogenation of the CO group to give phenylethanol ( $C_6H_5CHOHCH_3$ ) versus that of the aromatic ring to give acetylcyclohexane ( $C_6H_{11}COCH_3$ ). This system is complicated by secondary reactions that can give cyclohexylethanol ( $C_6H_{11}CHOHCH_3$ ), ethylbenzene ( $C_6H_5CH_2CH_3$ ) and ethylcyclohexane ( $C_6H_{11}CH_2CH_3$ ).

Our initial results are listed in Table 7 and the most significant aspects can be summarized as follows. Activities per g Pt and TOF's did not vary widely except for Pt/SiO<sub>2</sub>, which had noticeably lower values at an acetophenone pressure of 3 torr. The pure supports had almost immeasurable activities. Activation energies for overall acetophenone disappearance at the former pressure were low and ranged from 2 to 6 kcal/mole for all catalysts except Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; however, this probably

TABLE 6

CO Oxidation Kinetics on Au at Temperatures Below 100°C

Catalyst	Test Conditions			E <sub>a</sub> (kcal/mol)	Activity @ 40°C (μmol/s·g Au)	Ref.
	P (torr)		T (°C)			
	CO	O <sub>2</sub>				
1.8% Au/SiO <sub>2</sub>	38	37	40-85	3.3	3.85	This study
2.3% Au/TiO <sub>2</sub> (LTR)	39	37	35-80	0	0.33	This study
2.3% Au/TiO <sub>2</sub> (HTR)	38	37	45-90	1.4	12.20	This study
2.3% Au/TiO <sub>2</sub> (HTR)	7	3.5	35-75	3.5	3.57	This study
2.3% Au/TiO <sub>2</sub> (HTR-Calc.-LTR)	38	36	40-70	3.1	46.2	This study
	7.4	3.6	40	--	8.8	This study
Au Sponge	38	38	21-60	2.1	0.56	Cant et al.
5% Au/Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	7.6	752	58-190	7.2	2.6	Haruta et al.
12% Au/Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	7.6	752	70-0	--	21.3	Haruta et al.
12% Au/Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup> (Au/Fe=1/19)	7.6	3.8	30-75	7.9	0.8	Hoflund & coworkers
23% Au/CeO <sub>x</sub> <sup>a</sup> (Au/Ce=1/4)	7.6	3.8	30-75	7.3	0.6	Hoflund & coworkers
12% Au/MnO <sub>x</sub> <sup>a</sup> (Au/Mn=1/19)	7.6	3.8	30-75	2.0	3.4	Hoflund & coworkers

<sup>a</sup>Prepared by coprecipitation.

TABLE 7

## Kinetic Behavior of Vapor-Phase Acetophenone Hydrogenation over Pt

Catalyst	Runs with $P_A = 10$ , $P_{H_2} = 685$ torr				Runs with $P_A = 3$ , $P_{H_2} = 685$ torr			
	$E_a$ (kcal/mol)	$\mu\text{mol}/$ $\text{s} \cdot \text{g cat}$	$\text{mmol}/$ $\text{s} \cdot \text{g Pt}$	TOF ( $\text{s}^{-1} \times 10^3$ )	$E_a$ (kcal/mol)	$\mu\text{mol}/$ $\text{s} \cdot \text{g cat}$	$\text{mmol}/$ $\text{s} \cdot \text{g Pt}$	TOF ( $\text{s}^{-1} \times 10^3$ )
0.96% Pt/SiO <sub>2</sub>	a)	0.98	0.10	21	5.2 ± 2.2	0.18	0.02	4
	a)	1.2	0.13	25	5.0 ± 2.4	1.00	0.10	21
0.76% Pt/Al <sub>2</sub> O <sub>3</sub>	10.6 ± 1.4	2.1	0.27	51	6.3 ± 1.1	1.78	0.23	43
0.24% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> - I	13.4 ± 1.2	0.21	0.09	39	12.5 ± 2.5	0.22	0.09	40
0.24% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> - II	9.8 ± 3.1	0.25	0.10	46	10.9 ± 2.1	0.15	0.06	28
0.95% Pt/TiO <sub>2</sub> (LTR)	7.2 ± 1.3	1.57	0.17	44	2.3 ± 2.6 <sup>b</sup>	1.29	0.14	36
					3.6 ± 0.6 <sup>b</sup>	1.27	0.13	36
					3.5 ± 1.2 <sup>b</sup>	1.27	0.13	36
0.95% Pt/TiO <sub>2</sub> (HTR) - I	11.1 ± 1.6	0.95	0.10	---	6.2 ± 1.3	0.79	0.08	--
0.95% Pt/TiO <sub>2</sub> (HIR) - II	8.5	0.87	0.09	---	3.1 ± 1.1	0.78	0.08	--

a) Serious deactivation

b) Test with conversions of 50-70%

reflects the unique selectivity to ethylbenzene (ca. 90%) over this catalyst. This behavior is attributed to the high acidity of this silica-alumina support. The apparent activation energy was higher at the higher acetophenone pressure.

Selectivity was of particular interest, and the results in Figures 7a-7e show that, except for the acidic Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, phenylethanol was the predominant product even at conversions over 50% in many cases. The next most prevalent product was acetylcyclohexane, especially at lower conversions, but at higher conversions significant amounts of cyclohexylethanol were also present. Of special importance is the fact that the high temperature reduced (at 773K) Pt/TiO<sub>2</sub> (HTR) catalyst had the highest selectivity (80-90%) to hydrogenate the carbonyl bond only, and at higher conversions (above 40%) the decrease in selectivity was primarily due to the secondary reaction to further hydrogenate phenylethanol to cyclohexylethanol.

This pattern of an increase in selective activation of the carbonyl group is what we had predicted based on our earlier studies of acetone and crotonaldehyde hydrogenation. However, more study of this complicated reaction system is required to clarify the catalytic behavior. Mass transfer limitations at the higher conversions may be present due to capillary condensation; therefore, the kinetics of the secondary as well as the initial reactions need to be determined more quantitatively and the effect of temperature on selectivity is not yet known. Regardless, we are encouraged by these results because they provide more evidence that a judicious choice of a metal/support system can alter activity and selectivity in reactions that pertain to the production of specialty chemicals.

#### F. UHV Study of Pt/TiO<sub>2</sub> Systems

We have had a frustrating situation with our Leybold UHV system. It was delivered six months late in October, 1989, then, upon assembly, eight leaks developed after the initial bake-out. Seven were straightforwardly repairable but the last was found to be due to a bad seam weld in the main chamber, and Leybold had to disassemble the system and return the chamber for repair. After

reassembly and repair of the electron gun and XPS electronics, the system finally became ready for use this spring. Computer programs have been written for data collection and we are now mounting a 99.995% Pt foil to begin our initial study of the adsorbed states of CO and acetone.

### Personnel

During this period, Mohammed Rahaman completed his M.S. thesis on the hydrogenation of toluene and the xylenes over Pd catalysts, Shawn Lin started his PhD thesis on TiO-Supported Au and Pt catalysts, on which he is still working, and one B.S. ChE student conducted his senior research project on the kinetics of toluene hydrogenation over Pt catalysts. Dr. Daniel Barabino, from the University of Delaware, spent six months here as a postdoctoral fellow initiating some solid-state  $^{195}\text{Pt}$  NMR experiments, Professor S. Chen, from Fujian University in China, was a visiting scholar for a year studying acetone hydrogenation over Pt catalysts using our DRIFTS system, and Professor H.-W. Kim, from Kyungpook Sanup University in Korea, was a research associate for a year using both DRIFTS and conventional dispersive IR techniques to study benzene and toluene hydrogenation over Pd catalysts. Dr. Diane Sanders, from Iowa State University, will be joining us this summer to pursue studies of Au/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts.

### Publications

During the period covered by the present grant, 8 papers resulting from research sponsored by this DOE Grant were published, one is in press, and two are being prepared for submission. These publications are cited below; those noted by an asterisk pertain to results obtained since September, 1988. Copies of these papers are attached.

1. Vannice, M. A. and Sen, B., J. Catal. 115, 65 (1989), "Metal-Support Effects on the Intramolecular Selectivity of Crotonaldehyde Hydrogenation over Pt".
2. Chen, A. A., Benesi, A. J., and Vannice, M. A., J. Catal. 119, 14 (1989), "NMR Characterization of the Hydrogen and Deuterium Phases Present in Pd/SiO<sub>2</sub> Catalysts".



- \*3. Vannice, M. A., *J. Molec. Catal.* 59, 165 (1990), "The Use of "MSI" (Metal-Support Interactions) to Selectively Activate Carbonyl Bonds".
- \*4. Rahaman, M. V. and Vannice, M. A., *J. Catal.* 127, 251 (1991), "The Hydrogenation of Toluene and o-, m-, and para-Xylene over Pd: I. Kinetic Behavior and o-Xylene Isomerization".
- \*5. Rahaman, M. V. and Vannice, M. A., *J. Catal.* 127, 267 (1991), "The Hydrogenation of Toluene and o-, m-, and para-Xylene over Pd: II. Reaction Model".
6. Sen, B. and Vannice, M. A., *J. Catal.* 129, 31 (1991), "Enthalpy Changes During O<sub>2</sub> Adsorption and H<sub>2</sub> Titration of Adsorbed Oxygen on Pt".
7. Sen, B. and Vannice, M. A., *J. Catal.* 130, 9 (1991), "The Influence of Pt Crystallite Size on Heats of Adsorption of H<sub>2</sub> and CO and on CO Hydrogenation".
- \*8. Lin, S. and Vannice, M. A., *Catal. Lett.*, in press, "Gold Dispersed on TiO<sub>2</sub> and SiO<sub>2</sub>: Adsorption Properties and Catalytic Behavior in Hydrogenation Reactions".

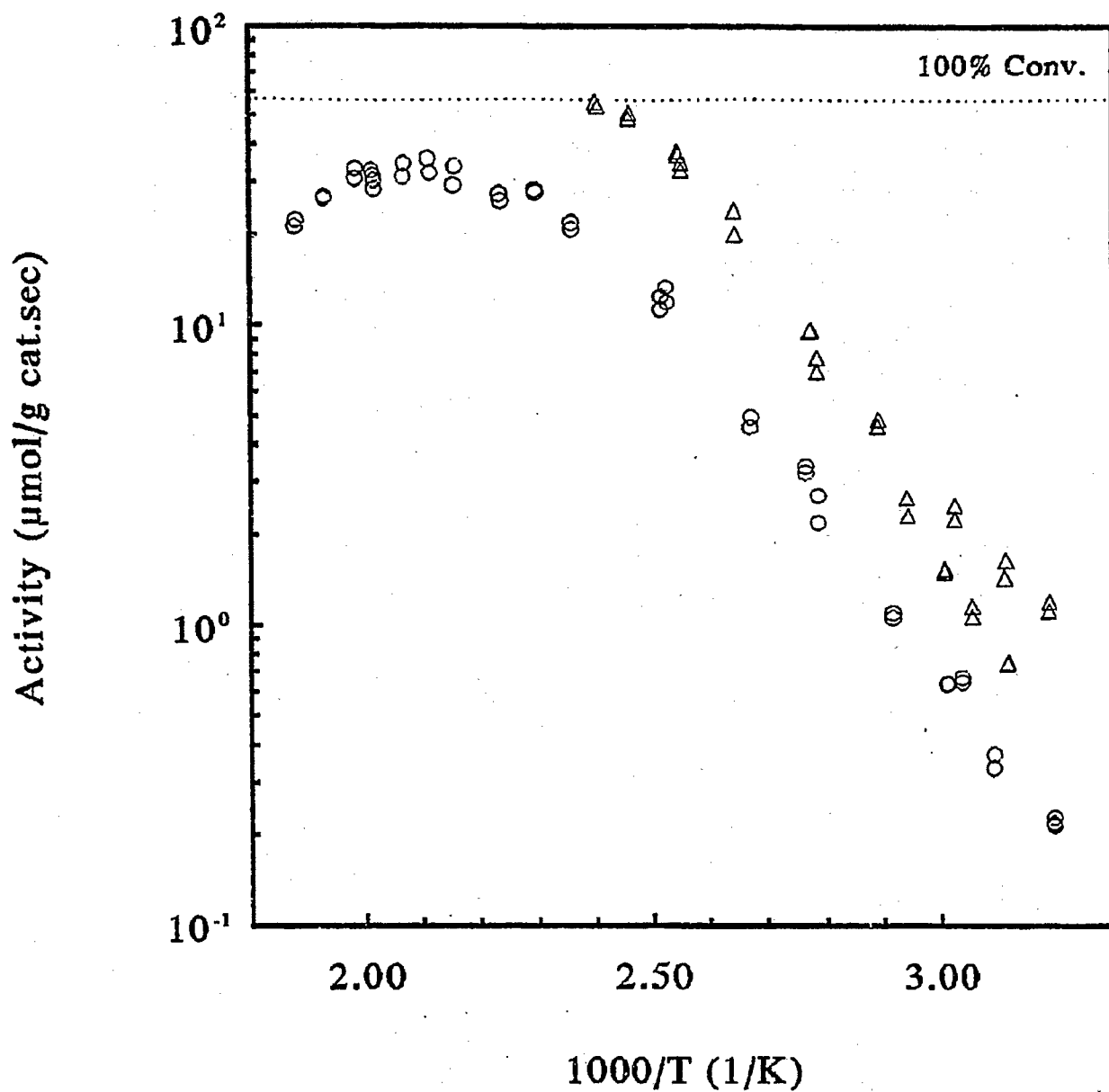


Figure 1: Arrhenius plots of benzene hydrogenation on 0.78% Pt/Al<sub>2</sub>O<sub>3</sub> over a wide temperature range: ○ - P<sub>Bz</sub> = 50, P<sub>H2</sub> = 680 torr, and Δ - P<sub>Bz</sub> = 35, P<sub>H2</sub> = 700 torr. Both runs used 0.4 g catalyst.

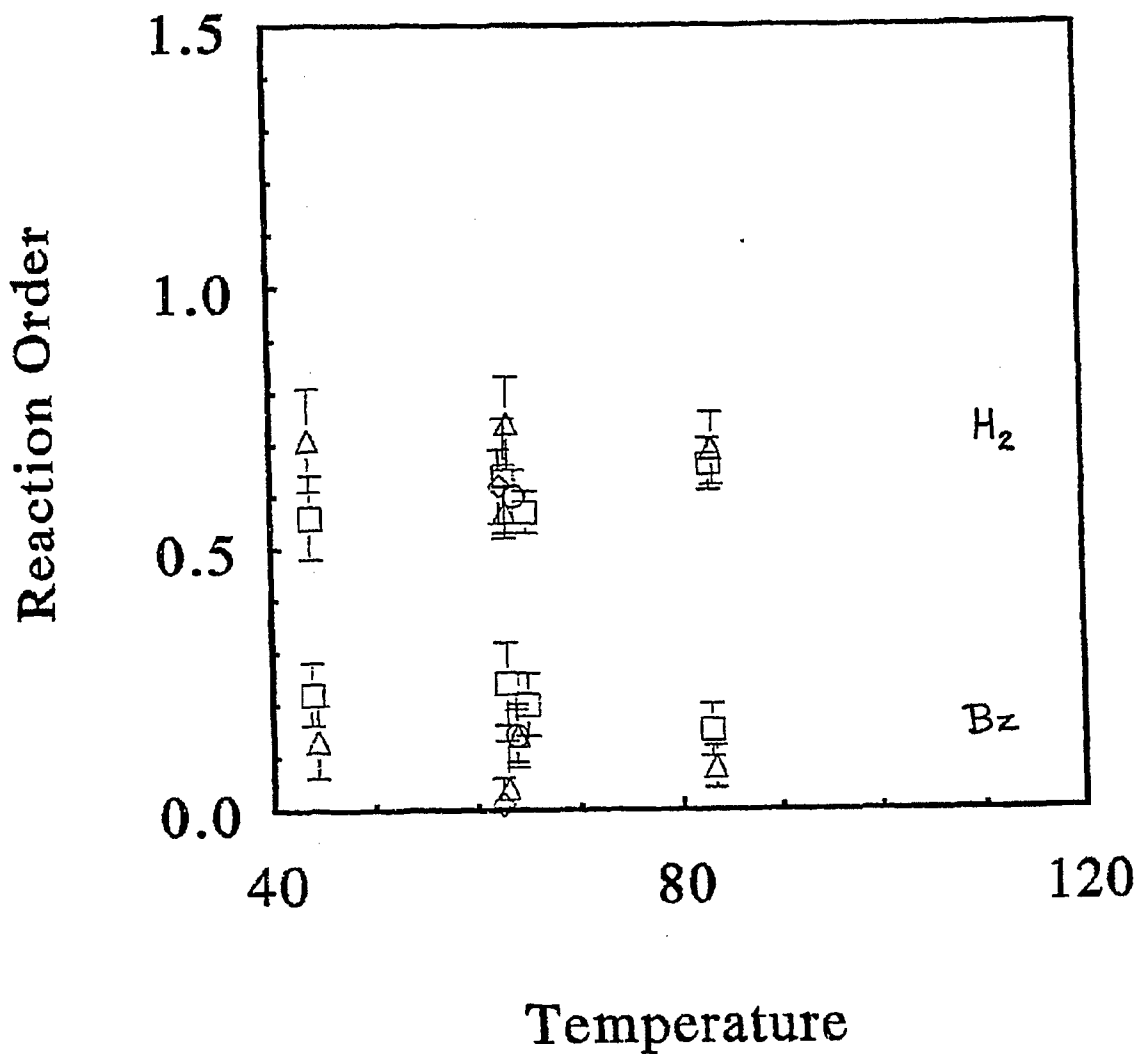


Figure 2: Partial pressure dependencies on benzene and H<sub>2</sub>: 0.24% Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> - Δ, 0.95% Pt/TiO<sub>2</sub> - ◇, 0.78% Pt/Al<sub>2</sub>O<sub>3</sub> - □, and 0.96% Pt/SiO<sub>2</sub> - ○. Error bars represent 95% confidence limits.

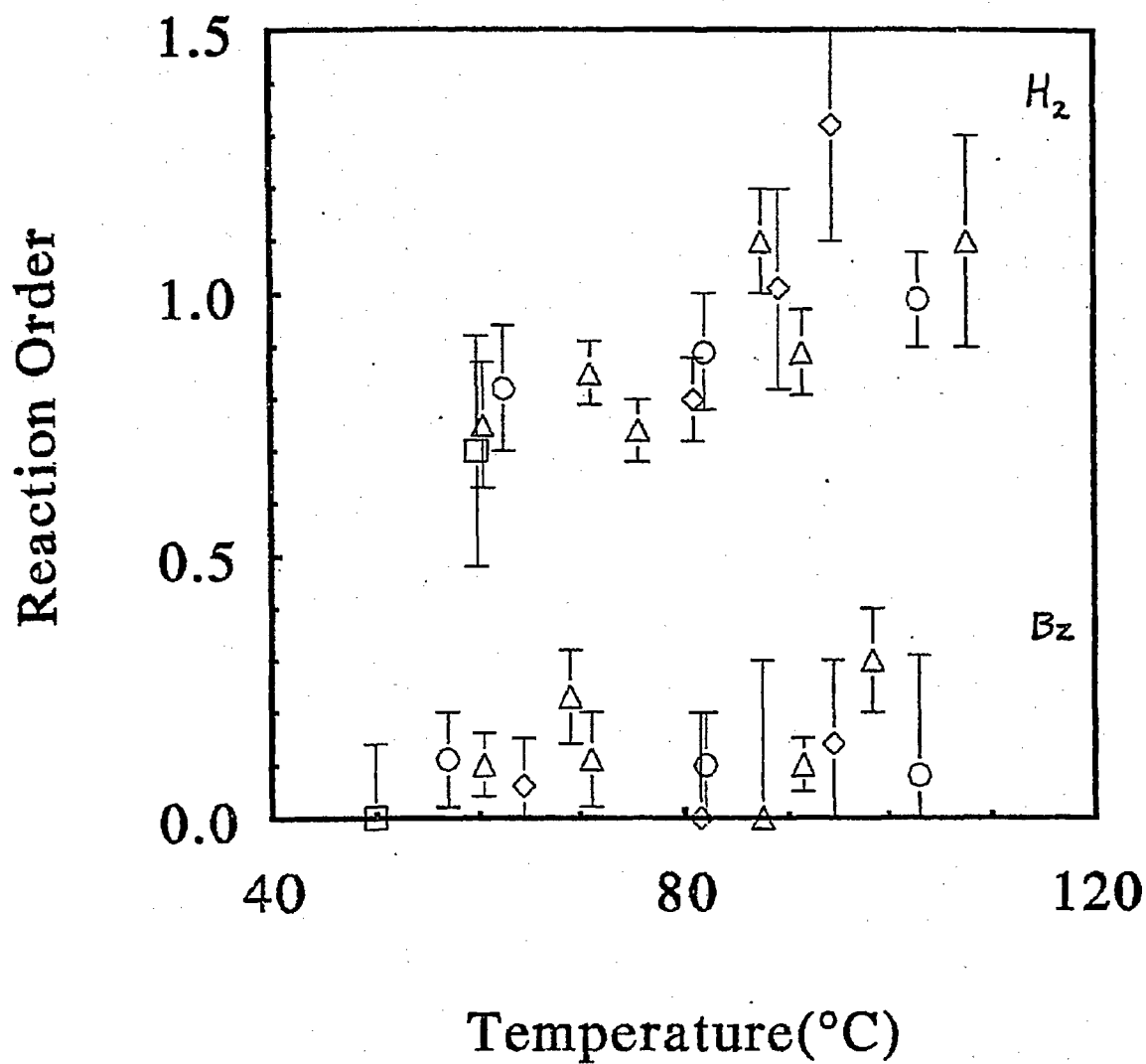


Figure 3: Partial pressure dependencies on toluene and H<sub>2</sub>: 0.24% Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> - Δ, 0.95% Pt/TiO<sub>2</sub> - ◇, 0.78% Pt/Al<sub>2</sub>O<sub>3</sub> - □, and 0.96% Pt/SiO<sub>2</sub> - ○. Error bars represent 95% confidence limits.

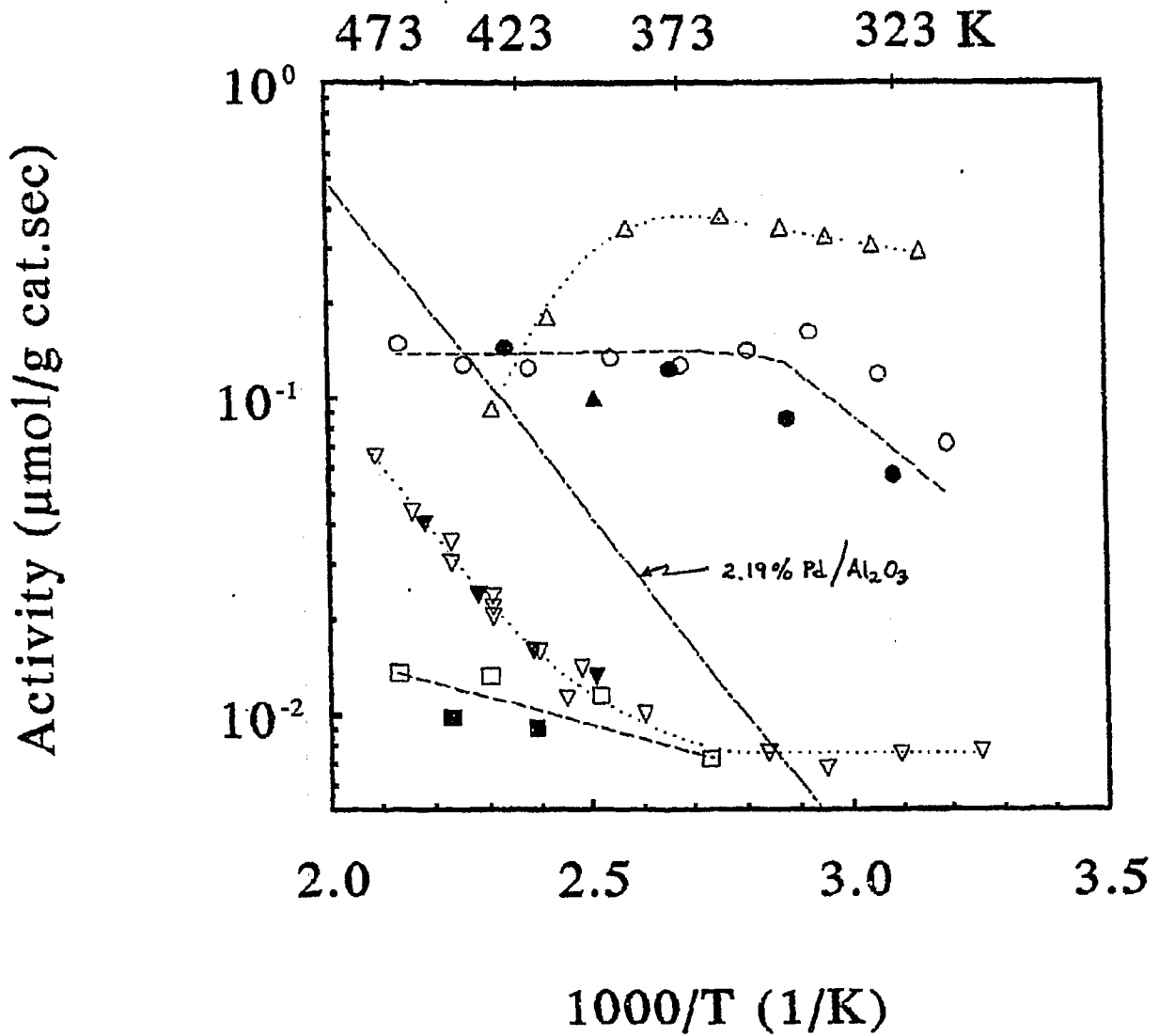


Figure 4: Arrhenius plots for CO oxidation at  $P_{\text{CO}} = P_{\text{O}_2} = 38$  torr, open symbols are from ascending and closed symbols are from descending temperature runs: 2.3% Au/TiO<sub>2</sub> (HTR) -  $\Delta$ , 2.3% Au/TiO<sub>2</sub> (LTR) -  $\nabla$ , 1.8% Au/SiO<sub>2</sub> - O, TiO<sub>2</sub> (HTR) only -  $\square$ .

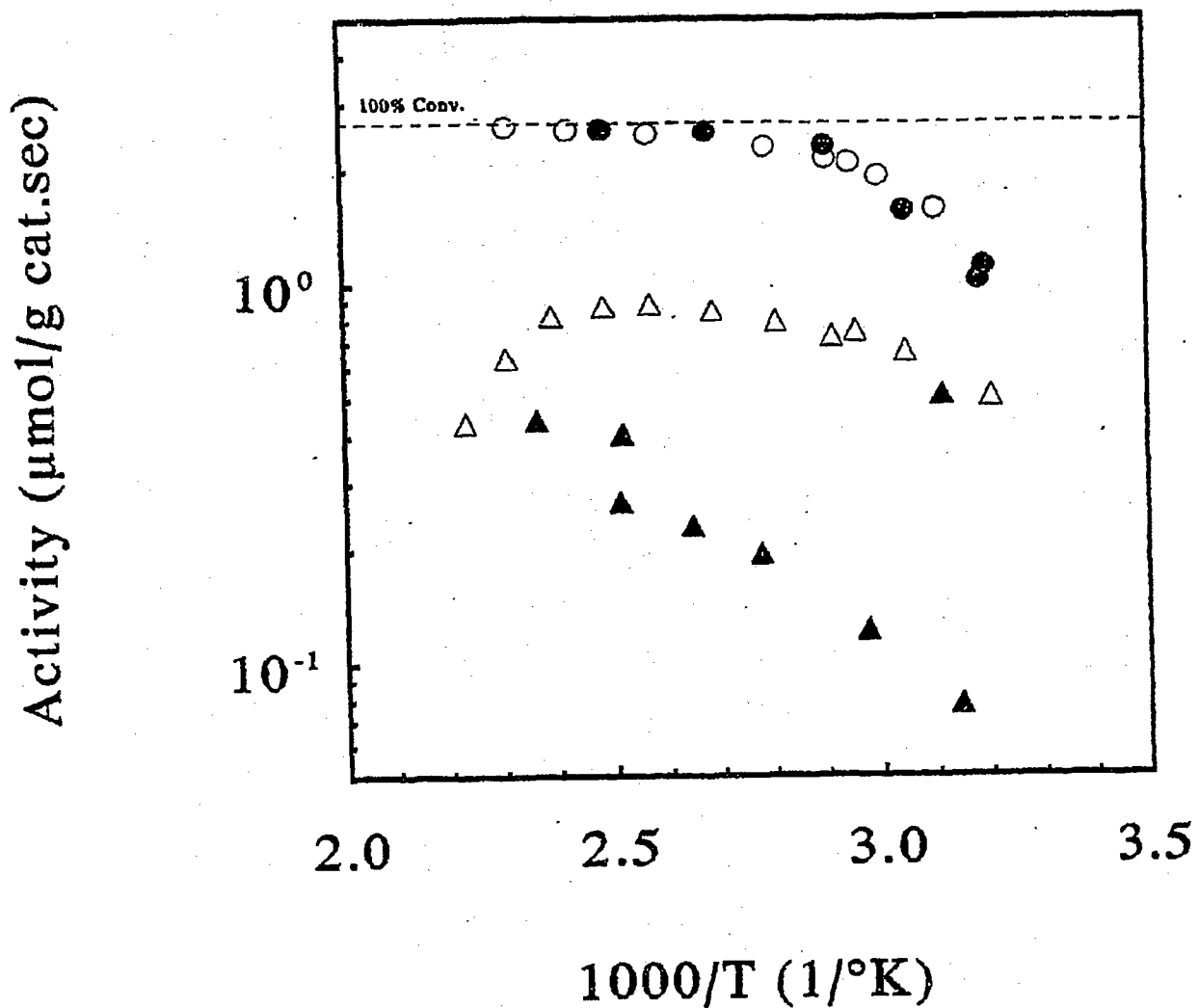


Figure 5: Pretreatment effect on CO oxidation activity for 23% Au/TiO<sub>2</sub>: LTR after calcination of HTR sample - O, HTR after slow admittance of O<sub>2</sub> - Δ. Open symbols are for ascending temperature and filled symbols are for descending temperature runs.

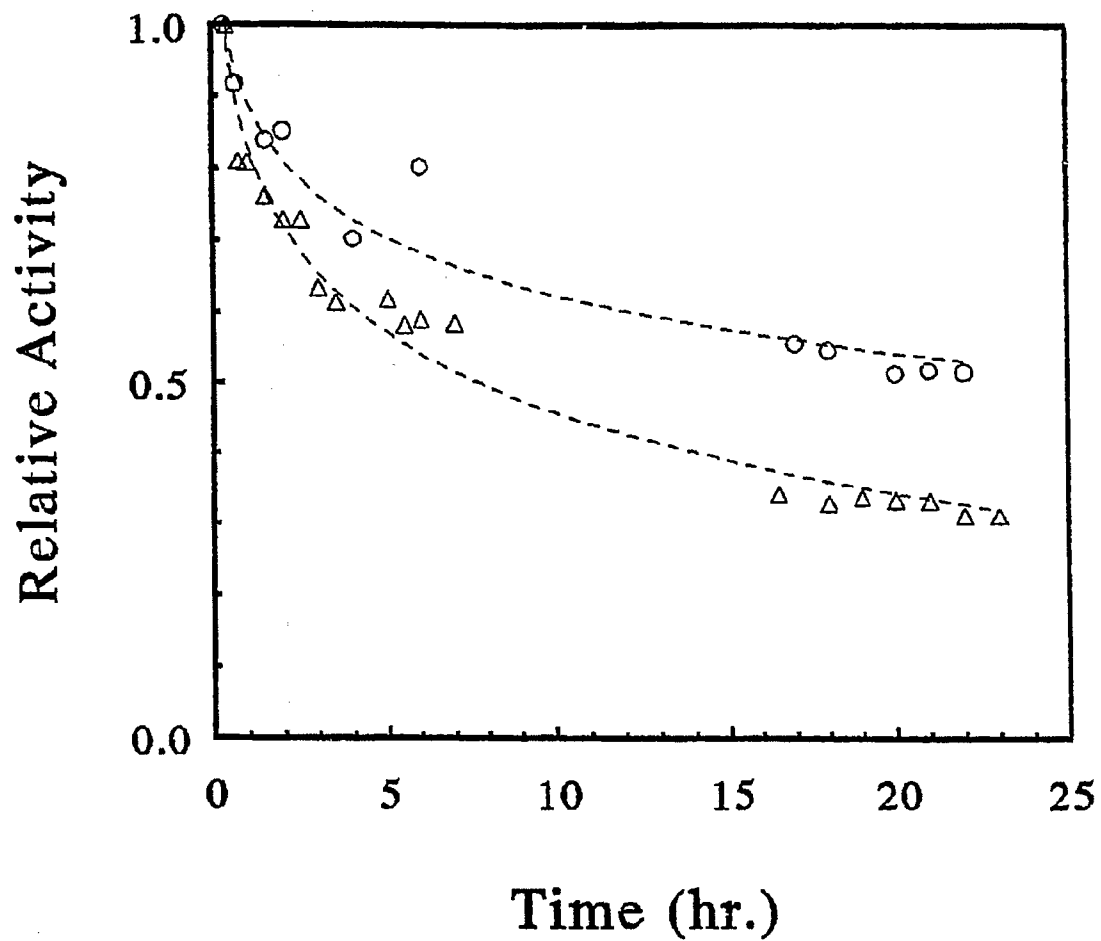


Figure 6(a): CO oxidation activity maintenance of 2.3% Au/TiO<sub>2</sub> after HTR at two partial pressure conditions: Δ - P<sub>CO</sub> = 38, P<sub>O<sub>2</sub></sub> = 37 torr, O - P<sub>CO</sub> = 7, P<sub>O<sub>2</sub></sub> = 3.5 torr.

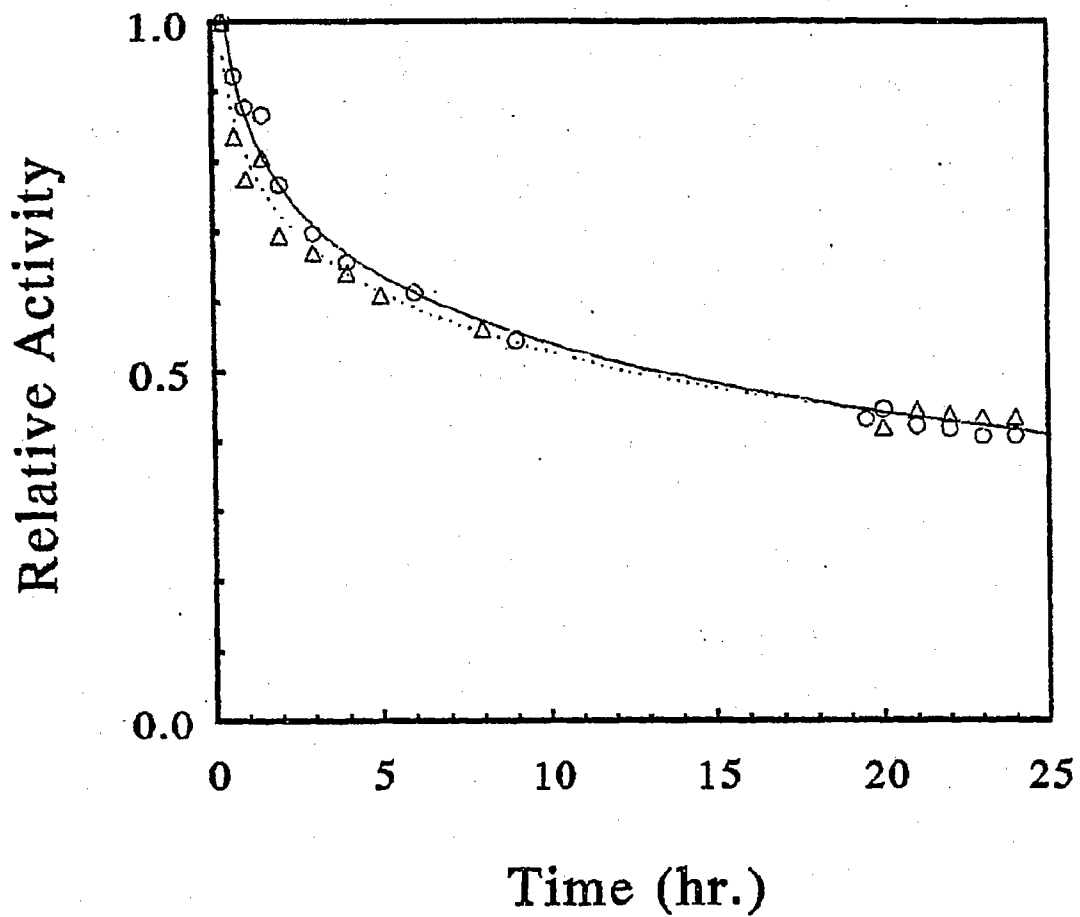


Figure 6(b): CO oxidation activity maintenance of 2.3% Au/TiO<sub>2</sub> after LTR following calcination of HTR sample at two partial pressure conditions: Δ - P<sub>CO</sub> = 38, P<sub>O<sub>2</sub></sub> = 37 torr, O - P<sub>CO</sub> = 7, P<sub>O<sub>2</sub></sub> = 3.5 torr.



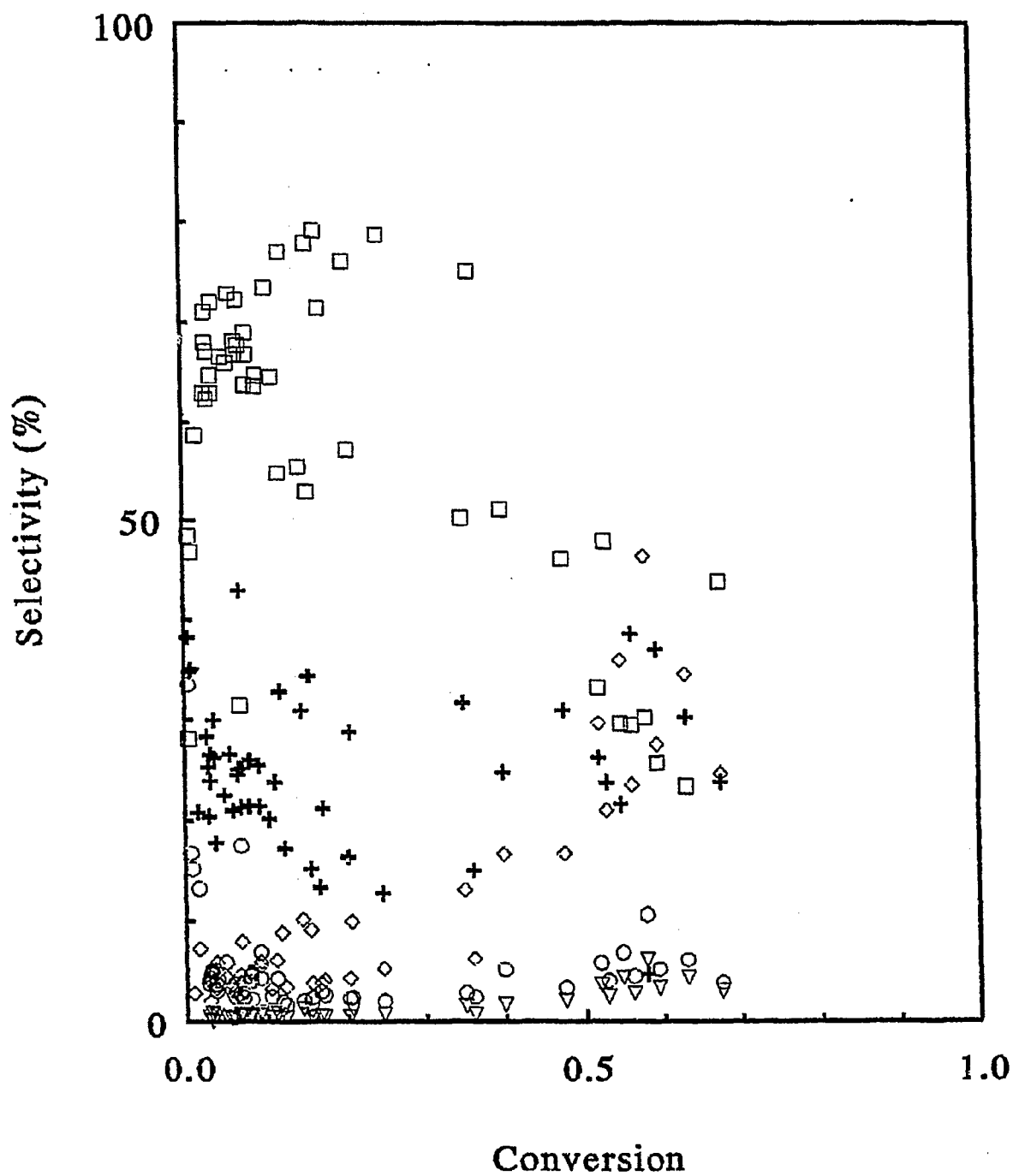


Figure 7(a): Selectivity vs. conversion of acetophenone over Pt/SiO<sub>2</sub>: Phenylethanol - □, Ethylbenzene - ○, Acetylcyclohexane - +, Cyclohexylethanol - ◇, and Ethylcyclohexane - ▽; P<sub>acetophenone</sub> = 10 torr, P<sub>H<sub>2</sub></sub> = 690 torr, T = 358-383K.

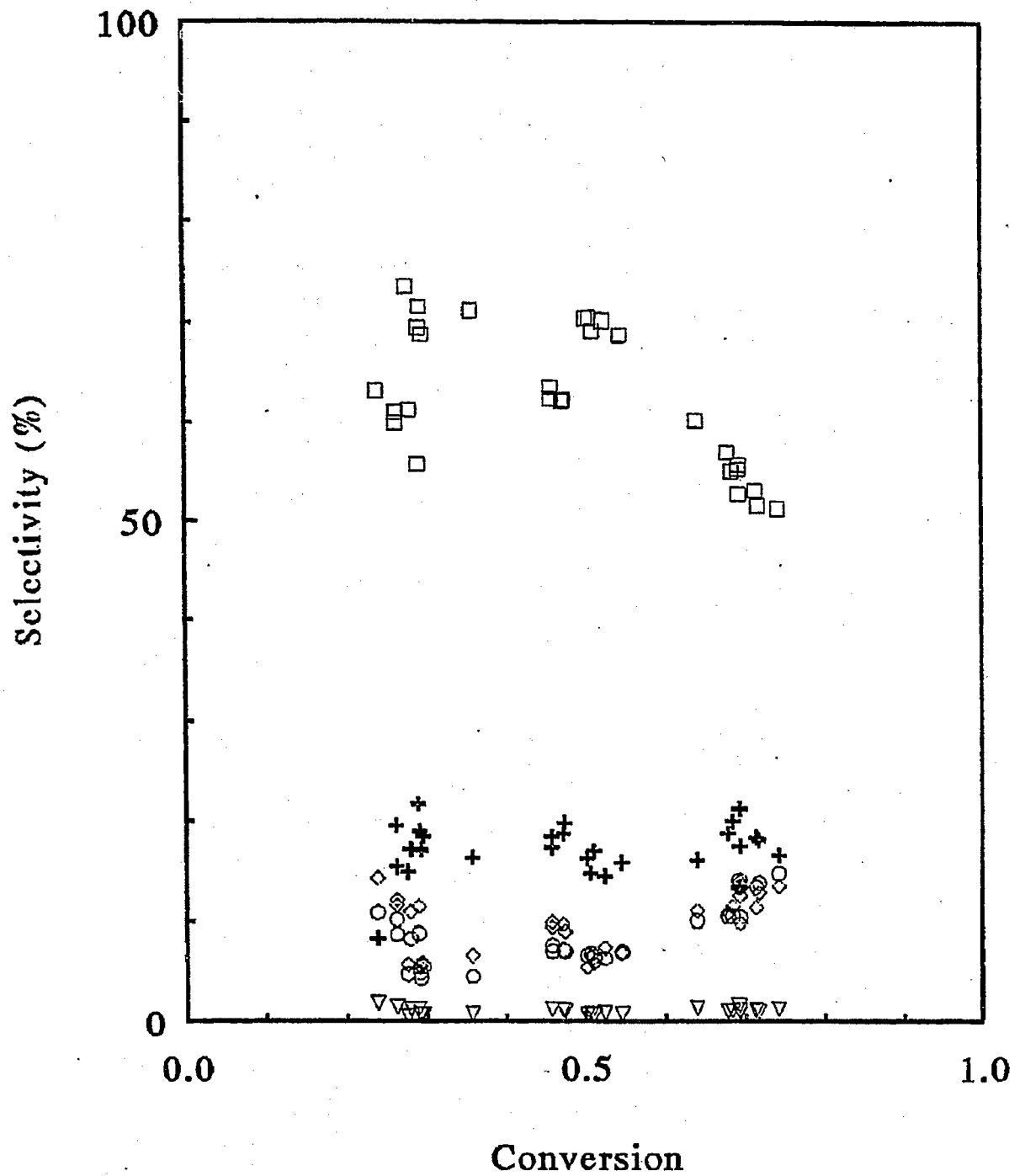


Figure 7(b): Selectivity vs. Conversion of Acetophenone over Pt/Al<sub>2</sub>O<sub>3</sub>: Phenylethanol - □, Ethylbenzene - ○, Acetylcyclohexane - +, Cyclohexylethanol - ◇, and Ethylcyclohexane - ▽; P<sub>acetophenone</sub> = 10 torr, P<sub>H<sub>2</sub></sub> = 690 torr, T = 358-383K.

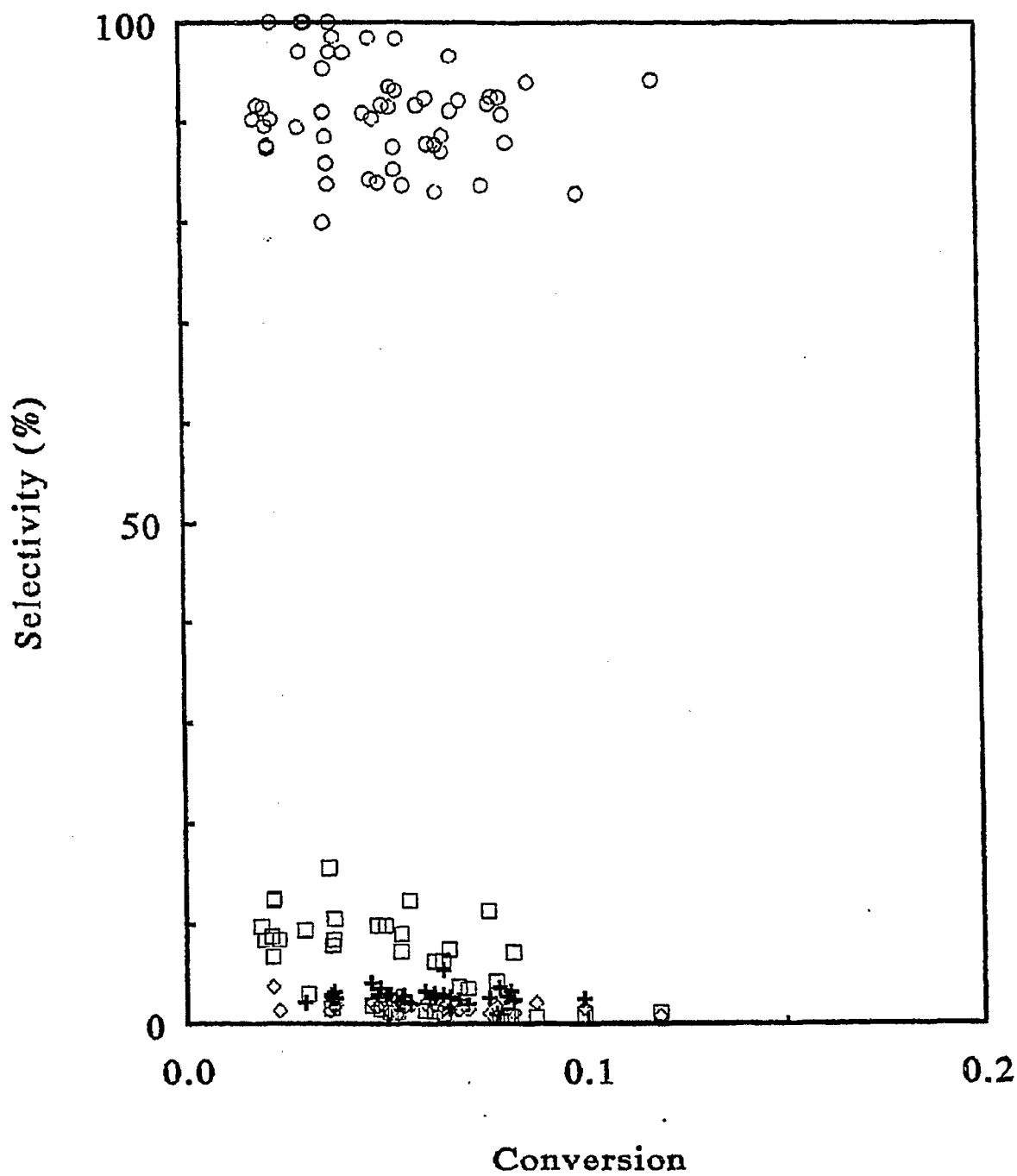


Figure 7(c): Selectivity vs. Conversion of Acetophenone over Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>: Phenylethanol - □, Ethylbenzene - O, Acetylcyclohexane - +, Cyclohexylethanol - ◇, and Ethylcyclohexane - ▽; P<sub>acetophenone</sub> = 10 torr, P<sub>H<sub>2</sub></sub> = 690 torr, T = 358-383K.

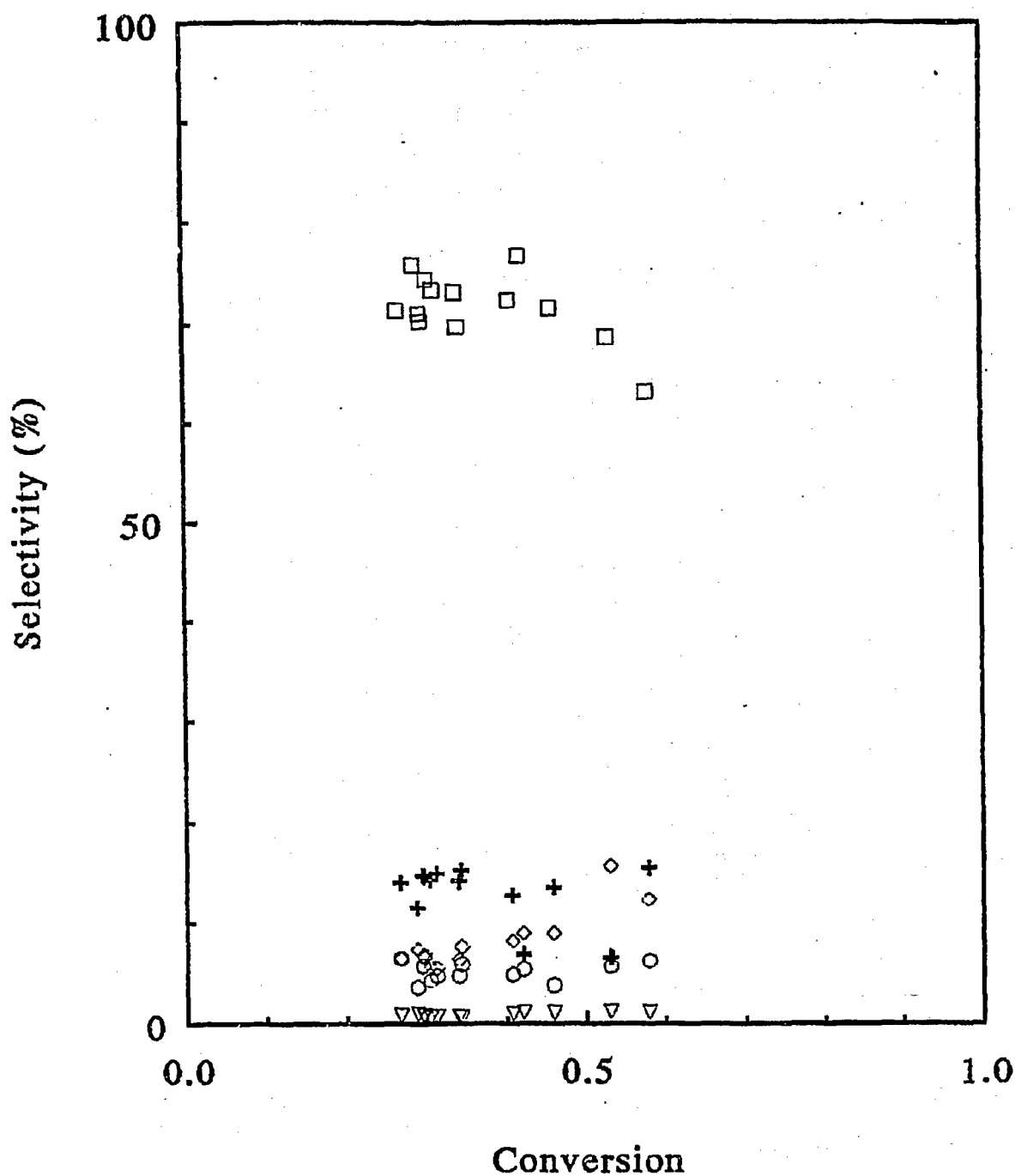


Figure 7(d): Selectivity vs. Conversion of Acetophenone over Pt/TiO<sub>2</sub> (LTR): Phenylethanol - □, Ethylbenzene - ○, Acetylcyclohexane - +, Cyclohexylethanol - ◇, and Ethylcyclohexane - ▽; P<sub>acetophenone</sub> = 10 torr, P<sub>H<sub>2</sub></sub> = 690 torr, T = 358-383K.

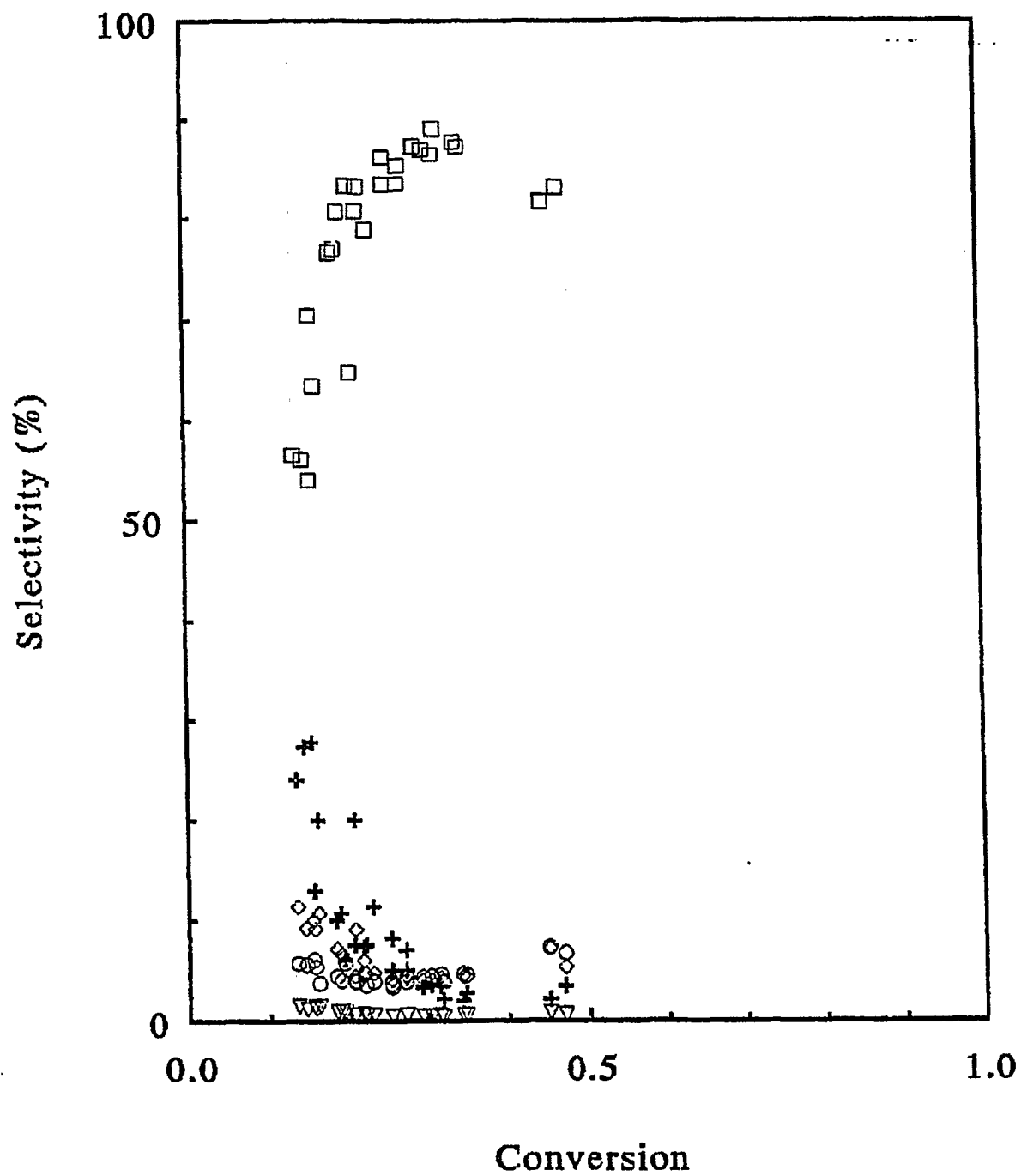


Figure 7(e): Selectivity vs. Conversion of Acetophenone over Pt/TiO<sub>2</sub> (HTR): Phenylethanol - □, Ethylbenzene - ○, Acetylcyclohexane - +, Cyclohexylethanol - ◇, and Ethylcyclohexane - ▽;  $P_{\text{acetophenone}} = 10 \text{ torr}$ ,  $P_{\text{H}_2} = 690 \text{ torr}$ ,  $T = 358\text{-}383\text{K}$ .