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CRYSTALLITE SIZE AND SUPPORT EFFECTS ON CO HYDROGENATION REACTIONS. FINAL PROGRESS REPORT, JANUARY 1, 1982-AUGUST 30, 1984

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

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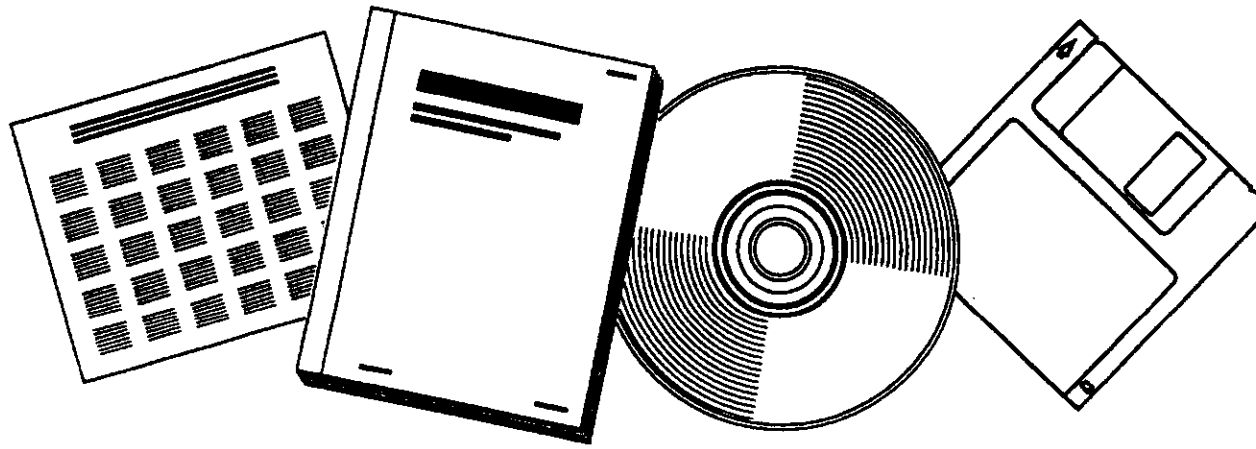

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CRYSTALLITE SIZE AND SUPPORT EFFECTS ON CO HYDROGENATION REACTIONS

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Summary of Research Program

By 1980 we had found that TiO_2-supported Pd was the most active Pd methanation catalyst yet reported, having turnover frequency (TOF) values nearly 100-fold higher than TOF's on Pd/SiO_2; however, our in situ IR studies showed that almost no IR-active CO was present on the Pd surface during reaction (1,2). During this time, similar results were found for Pt, as Pt/TiO_2 catalysts were found to be 100 times more active than Pt/SiO_2 catalysts and 10 times more active than Pt/Al_2O_3 and Pt/SiO_2-Al_2O_3 catalysts. Again surface concentrations of IR-active CO were barely detectable under reaction conditions (3-5). Because both H_2 and CO chemisorption measurements were conducted on these catalysts, we were able to develop a technique which allowed us to calculate for the first time separate IR extinction coefficients for the linearly-adsorbed and the bridged-bonded forms of CO on Pd and Pt surfaces (6,7). Using these coefficients, the surface concentrations of CO under reaction conditions could be estimated and these results indicated that only a small fraction (1-2%) of the TiO_2-supported metal surface was covered by CO. As a consequence, a modified model for the methanation reaction was proposed, and we inferred from our studies on Pt and Pd that only a small fraction of the surface metal atoms constitute "active sites" which create these higher activities (1,5,8).

The Pt catalysts were studied in greater detail by transient IR techniques. An IR cell with a very small dead volume was successfully built and transient experiments were conducted by stopping (or starting) the CO in the feed stream. Sharp rate maxima were obtained for Pt/Al_2O_3 and Pt/TiO_2 immediately after CO was removed from the feed stream and the rates then decayed as shown in Figures 1 and 2. The change in IR absorbance, A, is compared to that at steady-state, A_o. The rate maxima were very similar to

those obtained by others for Ru catalysts (9,10). Analyses are underway utilizing differential mass balance equations and CO surface concentrations from the IR spectra to test various kinetic models for methanation over Pt surfaces. The sharp rate increase upon removal of CO in the gas phase is consistent with our model involving hydrogen in the rate determining step (1,3), which has also been supported recently by Mori et al. (11).

Several explanations had been proposed to explain the higher activity of Ni/TiO_2 catalysts (12,13), and a study of physical mixtures of Pt/TiO_2 + Ni/TiO_2 catalysts plus a coimpregnated $Pt-Ni/TiO_2$ catalyst was conducted to test these models. We found that a synergistic effect occurred in all systems containing both Pt and Ni, and measured activities were up to three times greater than those predicted by summation of activities from the individual components (14). This enhancement was a consequence of higher Ni surface areas caused by the Pt-catalyzed reduction of the Ni salt at lower temperatures than typically required (200°C, for example). Hydrogen and CO chemisorption did not parallel this increase, and in a previous study we had found that equilibrium coverages on high temperature reduced TiO_2-supported Ni constitute only 1/4-1/3 of a monolayer (15). However, this same study indicated that oxygen chemisorption did not suffer this limitation and provided a satisfactory technique to measure Ni surface atoms when this metal-support effect occurred. When TOF values were calculated for these mixtures based upon surface Ni atoms determined by O_2 chemisorption, a constant TOF occurred showing that the reaction rate was proportional to the Ni surface area (14). Based upon this and other results from this study, we have been able to eliminate two possible explanations of this higher activity -- hydrogen spillover and higher (but undetected) Ni dispersion. Our results are consistent with a recent model proposed by Burch and Flambard that attributes the higher acti-

vity and shift in selectivity to special sites at the Ni-TiO_2 interface (16). However, an alteration of the "structure" of the Ni crystallites because of the support may also play a role in determining the relative types of surface carbon species, which would alter selectivity (12,14).

Only in this last study did the importance of the reduction temperature become apparent as a parameter. We, as essentially everyone else, had assumed that a high temperature reduction (HTR) was necessary for high activity as well as for suppressed chemisorption. However, our results showed that most of the enhanced activity with Pt/TiO_2 catalysts could be obtained after only a low-temperature reduction (LTR) of 200°C (5,14). This led us to also examine in great detail the effect of reduction temperature on catalytic activity for benzene hydrogenation in a family of Pd catalysts, and quite striking effects were found, as shown in Table 1 (17). The HTR which produces the suppressed chemisorption and high CO activity in these TiO_2-supported metal catalysts results in Pd/TiO_2 catalysts with normal activities whereas an LTR at 175°C results in Pd/TiO_2 catalysts with activities 5-10 times higher than typical Pd catalysts and our Pd/SiO_2-Al_2O_3 catalysts are the most active Pd catalysts yet reported. Although this is the first instance where a TiO_2- supported metal catalyst has produced higher than normal rates for a reaction other than CO hydrogenation, it definitely cannot be attributed to an "SMSI" effect, as shown in Figure 3. Activity plummets sharply with increasing reduction temperature while chemisorption decreases, as expected (17). A tentative model to explain this behavior is intriguingly similar to that proposed for CO hydrogenation (8) and is consistent with previous studies of benzene hydrogenation (17). We currently believe that acid sites present at the Pd-support interface enhance benzene adsorption in this adlineation reaction which increases the rates because of higher surface concentrations. Previous

studies have shown that benzene adsorbs on acid sites on the support (18), chloride is known to increase support acidity and this has recently been shown for TiO_2 (19). In agreement with this picture, we have found that chloride is needed to achieve these high activities, as shown in Table 2. Any chloride present in the Pd precursor salt may increase the acid site concentration in the region immediately surrounding the Pd crystallites during the pretreatment step. It should be emphasized that turnover frequencies on the most active Pd/SiO_2-Al_2O_3 catalysts are about 7 times higher than those on commercial Ni catalysts.

The kinetic properties of these TiO_2-supported metals coupled with the suppressed chemisorption suggested that this metal-support effect may alter the adsorbate-metal bond strength, and a major part of our program was oriented toward the measurement of heats of adsorption on these metal surfaces. A Perkin-Elmer differential scanning calorimeter was modified to allow its application to this problem. Heats of adsorption for both H_2 and CO on Pt have now been measured based on isothermal energy responses such as those shown in Figures 4 and 5, and the results are listed in Table 3. The dotted lines represent baseline behavior. These $\Delta H_{(a)}$ values are consistent with those previously reported in the literature for single crystal surfaces (20-22); however, very wide ranges of values have been reported for both CO and H_2 chemisorption on Pt (23). The highest values for both CO and H_2 occur on the Pt/SiO_2 catalysts and the values on Pt/TiO_2 are somewhat dependent on the number of reduction cycles. Initial ΔH_a values are similar to the other catalysts but decrease with repeated cycles. We believe that the apparent decline is due to the use of the initial chemisorption coverage and that additional portions of the Pt surface are covered by titania during cycling. This would also decrease chemisorption and would result in more constant ΔH_a values.

This is currently being verified. The important result, however, is that heats of adsorption do not appear to be markedly reduced on TiO_2-supported Pt indicating that blockage of adsorption sites is the principal reason for decreased chemisorption.

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Personnel, Publications and Presentations

During this period of time, Lori Hasselbring finished her M.S. Thesis entitled "Calorimetric Measurements of the Heats of Adsorption of H_2 and CO on Supported Pt Catalysts", Tom Leong is concluding his M.S. thesis entitled "Transient IR Studies of Methanation over Pt Catalysts", and Pen Chou has been working on his Ph.D. thesis entitled "Support Effects on Benzene Hydrogenation and H_2 and CO Adsorption on Pd". A new Ph.D. student, B. Sen, began his research last year on DSC/TGA studies of adsorption on Pt.

Publications during this period describing research sponsored by this project are:

Vannice, M. A., TiO_2-Supported Metals as CO Hydrogenation Catalysts, J. Catal. 74, 199 (1982).

Vannice, M. A. and Vasco-Jara, J., The Nature of Active Sites in SMSI Catalysts: Mixtures of Ni/TiO_2 and Pt/TiO_2, Studies in Surface Science and Catalysis, Metal-Support and Metal-Additive Effects in Catalysis, Elsevier, Vol. 11, p. 185 (1982).

Vannice, M. A., Support Effects in Nickel and Platinum CO Hydrogenation Catalysts, in "Pan-Pacific Synfuels Conference", Vol. 1, p. 208, Japan Petroleum Institute, Tokyo, 1982.

Vannice, M. A., Twu, C. C. and Moon, S. H., SMSI Effects on CO Adsorption and Hydrogenation on Pt Catalysts. Part I. In Situ IR/Kinetic Studies J. Catal., 79, 70 (1983).

Vannice, M. A. and Twu, C. C., SMSI Effects on CO Adsorption and Hydrogenation on Pt Catalysts. Part II. Kinetics of Methanation, J. Catal., 82, 213 (1983).

Vannice, M. A., Leong, T. and Sudhakar, C., "Methanation over Pt Catalysts", ACS Prepr., Div. Petr. Chem., accepted for publication (1984).

Chou, P. and Vannice, M. A., "The Influence of Pretreatment and the Support on Benzene Hydrogenation over Pd", 8th Int. Cong. on Catal., Berlin, accepted for publication (1984).

Vannice, M. A. and Sudhakar, C., "A Model for the Metal-Support Effect Enhancing CO Hydrogenation Rates over $Pt-TiO_2$ Catalysts", J. Phys. Chem., submitted for publication.

Vannice, M. A. and Hasselbring, L., "Integral Heats of Adsorption of CO and H_2 on Supported Pt", in preparation.

Finally, this research was described in papers given (or accepted for presentation) at 6 international meetings, 1 national ACS meeting, and 24 universities and laboratories.

Budget Statement

All funds will have been expended by the end of this grant.

Table 1

BENZENE HYDROGENATION OVER PALLADIUM

P_{Bz} = 50 torr, P_{H_2} - 680 torr, T = 140°C

Catalyst	T_R (°C)	E_a (kcal/mole)	Activity	
			μmole Bz·s^{-1}·gPd	TOF Bz(s^{-1})
2.0% Pd/SiO_2-Al_2O_3	175	14.2	2670	1.03
2.0% Pd/SiO_2-Al_2O_3 (c)	175	14.2	1730	0.50
2.0% Pd/SiO_2-Al_2O_3	400	11.7	381	0.14
1.8% Pd/Al_2O_3	175	12.6	436	0.12
1.8% Pd/Al_2O_3	400	12.4	313	0.10
10.3% Pd/Al_2O_3 (c)	400	13.1	22	0.067
1.7% Pd/SiO_2	175	12.2	108	0.15
1.7% Pd/SiO_2	400	11.3	35	0.043
1.4% Pd/C	400	8.5	4	0.003
Pd Powder	200	12.9	0.064	0.006

(c) - Calcined

Table 2

CATALYTIC BEHAVIOR OF BENZENE HYDROGENATION OVER TiO_2-SUPPORTED PALLADIUM

(P_{Bz} = 50 torr, P_{H_2} = 680 torr, T = 140°C)

Catalyst % Pd	T_R (°C)	E_a (kcal/mole)	Benzene Hydrogenation Activity: μmole Bz / s·g Pd	TOF Bz (s^{-1})
2.0	100	12.9	1260	0.48
2.0	175	12.3	926	0.64
2.0	250	12.3	141	0.11
2.0	320	12.4	98	0.082
2.0	400	11.9	62	0.077
2.0	500	11.3	25	0.071
2.0-(c)	175	14.2	1260	0.41
2.0-(O_2)	175	13.7	66	0.15
0.4	175	11.9	1590	0.52
1.9-(a,c)	175	14.1	132	0.14
1.9-(a,c,Cl)	175	13.7	1440	0.53
2.5-(n,c)	175	13.8	19	0.084

Table 3

ADSORPTION ON SUPPORTED PLATINUM

320K, 10% Gas, 90% Ar

Catalyst		Crystallite Size (nm)	$\Delta H_{(A)}$ (kcal/mole) H_2	CO
2.1% Pt/SiO_2	(A)	15	36	27
	(B)	6.7	34	32
1.5% Pt/SiO_2-Al_2O_3	(I)	2.9	29	23
	(II)	2.9	28	--
2.1% Pt/η-Al_2O_3		1.5	28	24
1.5% Pt/TiO_2 (LT)		1.1	21	20
1.5% Pt/TiO_2 (HT)	(I)	(~1.1)	3	--
	(II)	(~1.1)	3	23
	(III)	---	25	30
	(IV)	(~1.1)	33→6	40→30

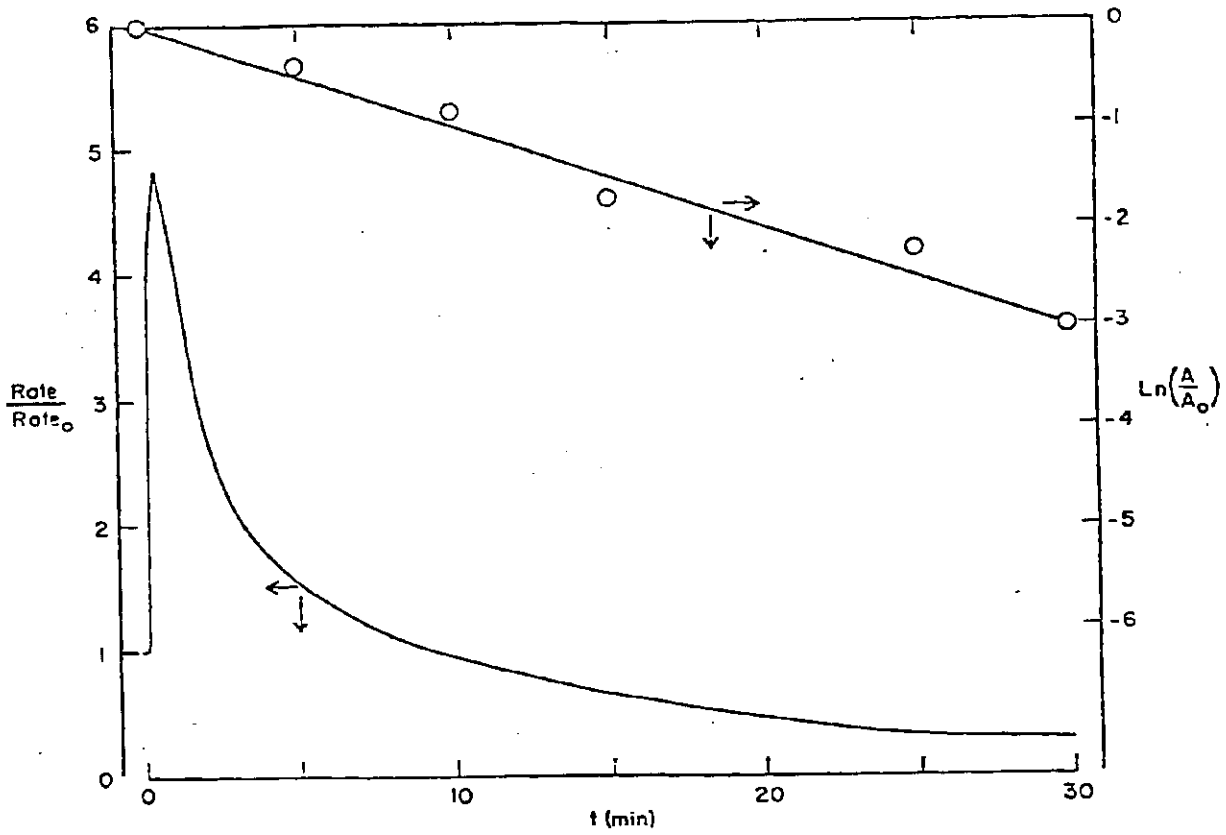


Figure 1 - The Variation with time of the Methanation Rate and Infrared Absorbance, A, at 548K over 1.8% Pt/Al_2O_3 Normalized to Values of Steady-State Reaction, after a Step-Change from 0.75 atm H_2 and 0.25 atm CO to 1 atm pure H_2.

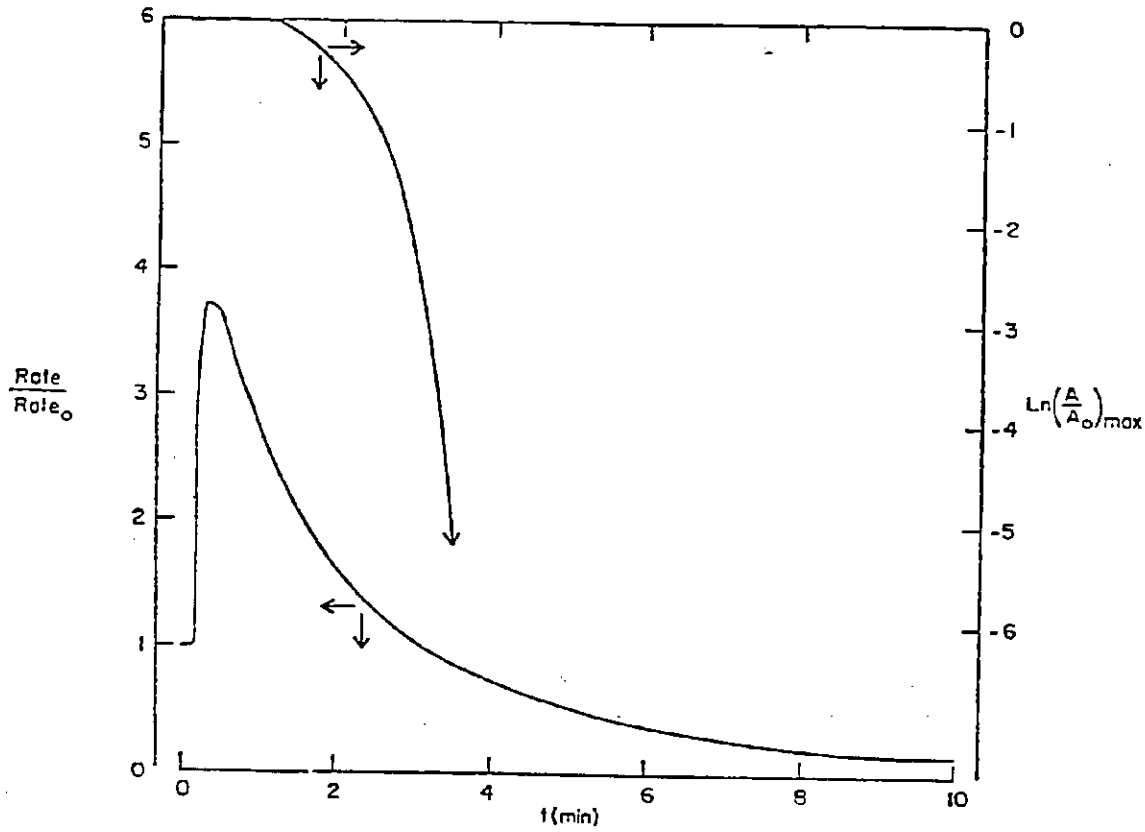
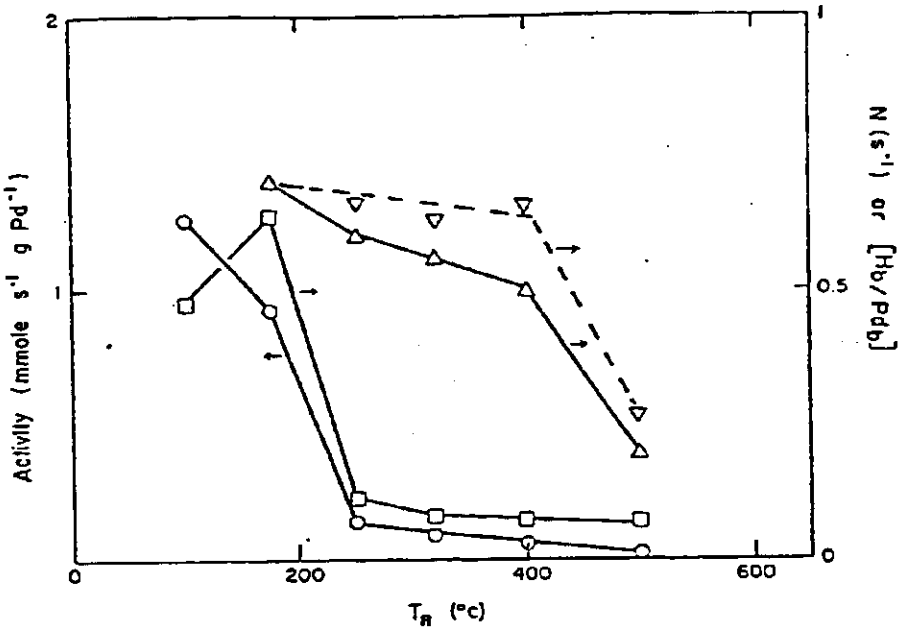


Figure 2 - The Variation with time of the Methanation Rate and Infrared Absorbance, A, at 548K over 1.9% Pt/TiO_2 Normalized to Values at Steady-State Reaction, after a Step-Change from 0.75 atm H_2 and 0.25 atm CO to 1 atm pure H_2.

Figure 3



Benzene Hydrogenation over 2.0% Pd/TiO_2 and Bulk Hydride Ratio versus Reduction Temperature. Reaction Conditions: T = 140°C, P_{H_2} = 680 torr, P_{Bz} = 50 torr. Activity - o; Turnover Frequency, N_{Bz} - □; Hydride ratio based on Pd_s measured by $H_{(ad)}$ - Δ; Hydride ratio based on assumption of constant Pd_s equal to that after T_R = 175°C - ∇.

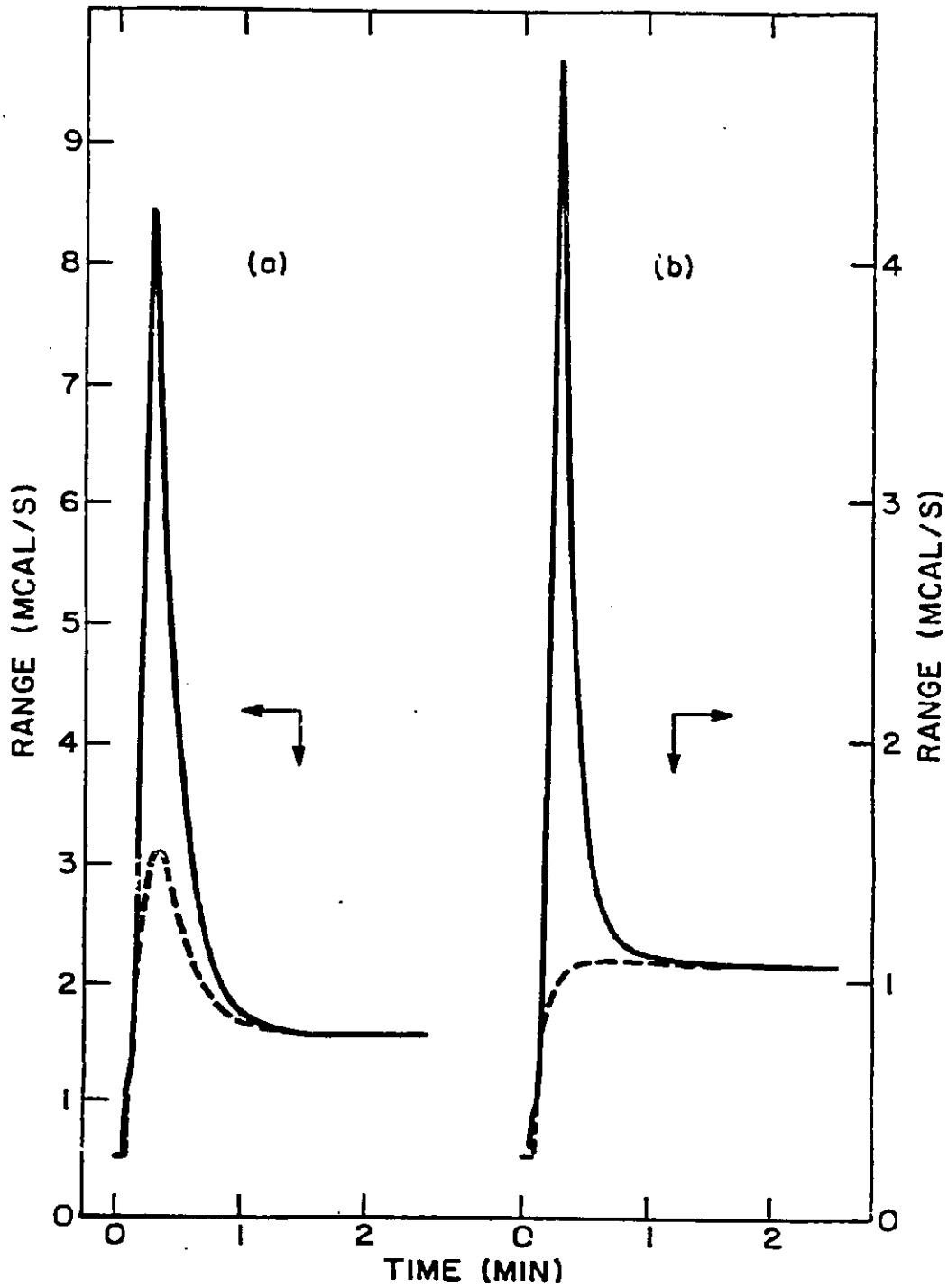


Fig. 4. Hydrogen DSC curves for 2.1% Pt/η-Al_2O_3 (Flow System II): (a) 320K; (b) 215K.

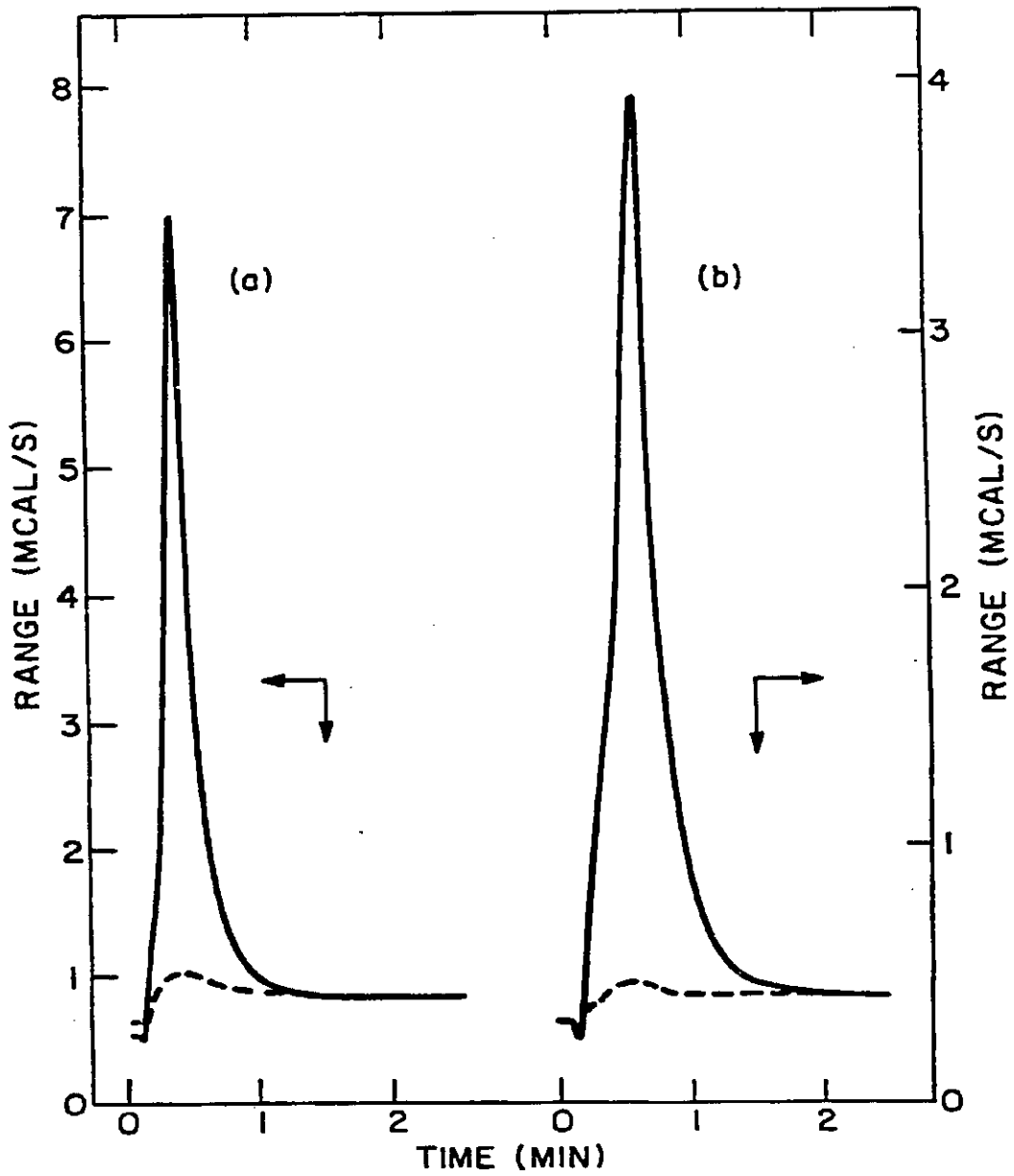


Fig. 5. Carbon monoxide DSC curves for 2.1% Pt/η-Al_2O_3 (Flow System II): (a) 320K; (b) 215K.