

# The Catalytic Synthesis of Hydrocarbons from H<sub>2</sub>/CO Mixtures over the Group VIII Metals

## III. Metal-Support Effects With Pt and Pd Catalysts

M. A. VANNICE

*Corporate Research Laboratories,  
Exxon Research and Engineering Company, Linden, NJ 07036*

Received April 29, 1975

Methane formation from CO/H<sub>2</sub> mixtures has been found to proceed much more rapidly on supported Pt and Pd than on unsupported Pt and Pd. Characterization of these catalysts by CO and H<sub>2</sub> chemisorption measurements allowed the determination of average particle sizes and specific activities. The enhancement of specific activity correlates with an increase in the surface concentration of the more weakly bound CO species. For Pt, this appears to be due primarily to a crystallite size effect, whereas for Pd the support plays the major role and infers a substantial metal-support interaction.

### INTRODUCTION

Transition metals are commonly placed on a variety of supports such as metal oxides. This is done not only to disperse the metal component, thereby increasing the number of surface metal atoms available for catalysis, but also to stabilize these small metal crystallites after they are formed. However, once a metal is dispersed on a support, the possibility exists that metal-support interactions can occur to alter the catalytic behavior of the metal (1-3). In principle these changes can occur not only because of the formation of very small metal crystallites which may possess different electronic and geometric properties compared to large crystals, but also from metal-support interactions which can result in electron transfer between the metal and support. Clearly defined metal-support effects are not plentiful but a number of examples have been reported which provide strong evidence that the support itself can alter the catalytic behavior of the metal component (4-8).

During the investigation of the catalytic behavior of supported Group VIII metals

for the synthesis of hydrocarbons from CO/H<sub>2</sub> mixtures, pronounced differences were observed with Pt and Pd which were dependent upon the support chosen to disperse the metal (9,10). Since the metal surface areas and dispersions of these catalysts had been determined, differences in specific activities were easily detectable. This paper discusses some of these results and offers an explanation to account for such changes in catalytic behavior.

### EXPERIMENTAL METHODS

The preparation of all catalyst samples has been described earlier except for samples B, C, and D. Sample B was prepared by impregnating SiO<sub>2</sub>, in the form of Cab-O-Sil obtained from the Cabot Corp., with an aqueous solution of chloroplatinic acid using an incipient wetness technique. Sample C was prepared with the same metal loading by soaking Cab-O-Sil in an aqueous solution of Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> while the pH was maintained at 10 by the addition of NH<sub>4</sub>OH. Both samples were dried in air for 16 hr at 120°C. Sample D was prepared by physically mixing together Pt

black and powdered  $\eta$ - $\text{Al}_2\text{O}_3$ . The Pt particle size of catalyst A' was increased by sintering Catalyst A in dry air for 4 hr at 700°C. The Pd crystallite size on  $\text{Al}_2\text{O}_3$  was varied by sintering catalysts G and H for 2 hr in hydrogen at 700°C.

All supported catalyst samples were characterized by CO chemisorption, and also  $\text{H}_2$  chemisorption when possible, to measure metal surface areas and determine metal dispersion values. The procedure for chemisorption measurements has been described previously (9). The metal surface area of the Pt black sample was measured by  $\text{H}_2$  adsorption only and that of the Pd black sample was measured by CO adsorption only. The Pt surface area in the physical mixture was determined using both CO chemisorption and the  $\text{O}_2$ - $\text{H}_2$  titration technique (11). To be consistent with earlier studies, an adsorbed CO molecule on the metal surface is assumed to define an active site for specific activity calculations. An adsorbed H atom could be used equally well—this would reduce

$N_{\text{CH}_4}$  values by a factor less than 2 but would not alter the trends observed in relative activities.

Kinetic data were obtained from a differential flow reactor, operated under steady-state conditions, where CO conversions were maintained at very low levels—normally between 0.2–2% as listed in Tables 2 and 3. At these low conversions, the turnover number for methane formation,  $N_{\text{CH}_4}$ , was independent of space velocity. In addition, application of the Koros-Nowak criteria also revealed no significant change in  $N_{\text{CH}_4}$  (12). Both tests indicate the absence of diffusional limitations. Techniques and procedures used have been described in detail elsewhere (9,10).

## RESULTS AND DISCUSSION

The chemisorption data and calculated metal dispersions are listed in Table I. The dispersion values of the fresh reduced catalysts are listed when available. In each case, the decrease in available metal sur-

TABLE I  
CHEMISORPTION DATA FOR USED CATALYST SAMPLES

Catalyst	CO uptake ( $\mu\text{mole/g}$ )	$\text{H}_2$ uptake ( $\mu\text{mole/g}$ )	% Dispersion		
			Based on $\text{CO}^a$	Based on $\text{H}_2$	Of fresh sample
(A) 1.75% Pt/ $\text{Al}_2\text{O}_3$	39.5	32.5	88	72	100
(A') 1.75% Pt/ $\text{Al}_2\text{O}_3$ (sint.)	7.1	8.4	16	19	—
(B) 2.0% Pt/ $\text{SiO}_2$ (I)	23	—	45	30	63
(C) 2.0% Pt/ $\text{SiO}_2$ (E)	35	38	68	74	100
(D) 25% Pt black/ $\text{Al}_2\text{O}_3$ (physical mixture)	1.6	5.3 <sup>b</sup>	0.25	0.27	—
(E) Pt black	—	8	—	0.3	—
(G) 2% Pd/ $\text{Al}_2\text{O}_3$	20.8	—	22	—	39
(H) 9.5% Pd/ $\text{Al}_2\text{O}_3$	12.6	—	13	—	—
(I) 0.5% Pd/H-Y Zeolite	38.2 <sup>c</sup>	—	8.6	—	—
(J) 4.75% Pd/ $\text{SiO}_2$	8	—	34	—	100
(K) 4.75% Pd/ $\text{SiO}_2$	84.8	58 <sup>d</sup>	38	26	46
(L) 4.75% Pd/ $\text{SiO}_2$	51	—	23	—	46
(L) Pd black	24	—	0.5	—	—

<sup>a</sup> Assuming bridged bonding.

<sup>b</sup>  $\text{O}_2$ - $\text{H}_2$  titration.

<sup>c</sup> Uptake on fresh sample.

<sup>d</sup> Uptake @ 70°C and 1 Torr.

TABLE 2  
 KINETIC BEHAVIOR OF Pt CATALYSTS<sup>a</sup>

Catalyst	$N_{\text{CH}_4}$ @ 275°C ( $\text{sec}^{-1} \times 10^3$ )	$E_m$ (kcal/mole)	$D_{\text{av}}$ (Å)	CO conversion (%)
(A) 1.75% Pt/Al <sub>2</sub> O <sub>3</sub>	2.7	16.7 ± 0.8	12	1.5–3.0
(A') 1.75% Pt/Al <sub>2</sub> O <sub>3</sub>	2.2	—	57	0.2–0.5
(B) 2.0% Pt/SiO <sub>2</sub> (I)	1.6	—	23	0.2
(C) 2.0% Pt/SiO <sub>2</sub> (E)	1.6	—	16	0.5
(D) 25% Pt black/Al <sub>2</sub> O <sub>3</sub> (physical mixture)	0.018	23	4300	0.01–0.04
(E) Pt black	No detectable activity <0.02	—	3600	—

<sup>a</sup> H<sub>2</sub>/CO = 3; *P* = 1 atm; 1 kcal = 4184 J.

face area can be reasonably attributed to sintering of the metal crystallites. Even so, in most cases the change in dispersion is not great. The kinetic behavior of these catalysts in the methanation reaction is shown in Tables 2 and 3 with specific activities represented as turnover numbers (molecules/site sec). All kinetic data were obtained at a H<sub>2</sub>/CO mole ratio of 3.

To provide a measurement of activity in more conventional terms, the turnover number of 0.01 for Catalyst H corresponds to ~30 cc CH<sub>4</sub>/hr · cc catalyst. This compares to ~300 cc CH<sub>4</sub>/hr · cc catalyst at 250°C for a typical Raney nickel catalyst. However, perhaps a fairer comparison is the activity per gram of metal

which is 840 cc CH<sub>4</sub>/hr · g Pd versus 140 cc CH<sub>4</sub>/hr · g Ni.

It is quite clear from Tables 2 and 3 that dispersing Pt or Pd on the appropriate support markedly enhances its specific activity. Placing Pt on Al<sub>2</sub>O<sub>3</sub> increases its specific activity by over 2 orders of magnitude compared to unsupported Pt. With Pd on Al<sub>2</sub>O<sub>3</sub>, the enhancement over unsupported Pd at 275°C is calculated to be a factor of 80 while at 345°C it is a factor of 40. The physical mixture of Pt black/Al<sub>2</sub>O<sub>3</sub> was prepared and examined not only to eliminate the possibility of channeling in the catalyst bed but also to provide a getter for any impurities which may have been present in the feed stream since it has been

 TABLE 3  
 KINETIC BEHAVIOR OF Pd CATALYSTS<sup>a</sup>

Catalyst	$N_{\text{CH}_4}$ ( $\text{sec}^{-1} \times 10^3$ )		$E_m$ (kcal/mole)	$D_{\text{av}}$ (Å)	CO conversion (%)
	275°C	345°C			
(F) 2% Pd/Al <sub>2</sub> O <sub>3</sub>	12	92 <sup>b</sup>	19.7 ± 1.6	48	1.1–2.5
(G) 2% Pd/Al <sub>2</sub> O <sub>3</sub>	7.4	—	23.6 ± 1.9	82	0.6–2.7
(H) 9.5% Pd/Al <sub>2</sub> O <sub>3</sub>	10	—	21.0 ± 0.8	120	0.6–1.6
(I) 0.5% Pt/H-Y Zeolite	5.9	52 <sup>b</sup>	21.2 ± 3.1	31	0.2–0.6
(J) 4.75% Pd/SiO <sub>2</sub>	0.32	5.0 <sup>c</sup>	26.9 ± 1.8	28	0.2–0.6
(K) 4.75% Pd/SiO <sub>2</sub>	0.26 <sup>c</sup>	4.1	—	46	1.2
(L) Pd Black	0.15 <sup>c</sup>	2.3	—	2100	1.0

<sup>a</sup> H<sub>2</sub>/CO = 3, *P* = 1 atm.

<sup>b</sup> Calculated using appropriate  $E_m$  value.

<sup>c</sup> Calculated using  $E_m = 26.9$  kcal/mole.

shown that impurities can effect certain reactions (13). As mentioned in the Experimental Methods section, no evidence of diffusional limitations was found at these low conversions.

No significant change in product selectivity was noticed. Both Pt and Pd, especially Pd, are very selective methanation catalysts (9). However, with either Pt or Pd, increasing the acidity of the support results in an increase in the methane turnover number. With Pt the most dramatic change occurs when the dispersion is greatly increased regardless of the support used. An increase in the dispersion by a factor greater than 200 increases the *specific activity* by two orders of magnitude. Varying the support changes the specific activity by a factor less than 2. Because of this, the major increase in specific activity for Pt is attributed to a crystallite size effect rather than a metal-support interaction involving electron transfer between the Pt particles and the oxide on which they are dispersed. In support of this, a recent review of chemisorption by Freil (14) indicates that CO adsorbs in a bridged structure on large Pt crystallites; however, on small Pt clusters the linear form of CO predominates and this structure is less strongly bound to the bridged form. The preponderance of the linear form on highly dispersed Pt on alumina has been clearly demonstrated by Darensbourg and Eischens (15) and by Kikuchi *et al.* (16). It has been shown in an earlier part of this study that a decrease in the bond strength of adsorbed CO could be predicted to result in an increase in specific activity for methanation (10). This shift to a less strongly adsorbed form of CO due to a decrease in Pt crystalline size (to  $\sim 2$  nm or less) appears to be the most of reasonable, and the simplest, explanation of the observed rate enhancement for methanation over supported Pt.

Although the methane turnover number decreased only 20% as the Pt particle size grew to 6 nm, the trend is consistent with

that predicted, i.e., that  $N_{\text{CH}_4}$  is lower on large Pt crystallites. The absence of a large decrease in activity, which might be expected as the average particle size grows from 1.2 to 6 nm (17,18), is quite possibly due to the presence of crystalline planes other than the (111) face which is favored to predominate on large Pt crystallites. Exposure to oxygen followed by hydrogen reduction has been shown to enhance hydrogen adsorption and increase the amount of linearly adsorbed CO (15,16). This effect has been attributed to either surface rearrangement or an increase in metal surface area or both together. Since catalyst A' was subjected to a high temperature exposure to oxygen prior to hydrogen reduction, unduly roughened Pt surfaces might be expected to exist thereby maintaining the relatively high activity of 6 nm Pt crystallites on alumina.

In contrast, the Pd catalysts do not show such a clear-cut dependence on particle size. Although it is apparent that *any* supported Pd catalyst has a higher specific activity than unsupported Pd, an increase in dispersion approaching 2 orders of magnitude does not necessarily result in a large increase in  $N_{\text{CH}_4}$  as found with Pt. For instance, this can be seen by comparing Catalysts F and K. Here the support seems to play a much more important role with the most active catalysts again being those utilizing the most acidic support. However, the increase in activity can still be related to an increase in the surface concentration of the more weakly bound CO species. Analogous to Pt, infrared studies of CO adsorbed on Pd have indicated that a shift from a strongly bound species to a less strongly bound species occurs as the particle size decreases (18-20). Figueras and co-workers (7) examined the ir spectra of CO adsorbed on a variety of Pd catalysts and found evidence that an increase in support acidity produced an enhancement of the ir band assigned to linearly adsorbed CO. They attributed this to a decrease in the electron density of the

Pd crystallites. Van Hardeveld and Hartog (18) found that the more weakly bound CO species was enhanced by either the formation of small Pd crystallites or by the use of an alumina support, compared to silica. For the SiO<sub>2</sub>-supported samples, the more weakly bound CO was dominant only for 1.5 nm Pd particles, whereas for 4.5 and 10.5 nm particles on SiO<sub>2</sub> the surface was predominantly covered with the strongly bound species. However, for Pd on Al<sub>2</sub>O<sub>3</sub>, the weakly bound CO dominated on Pd crystallites up to 11.5 nm while nearly equal coverages of each CO species existed on 19 nm crystallites (18). Such an effect might explain why the sintered Pd/Al<sub>2</sub>O<sub>3</sub> catalysts retained most of their specific activity even though average crystallite sizes increased to greater than 12 nm.

It seems, therefore, that methanation activity is increased by any effect which enhances the formation of the more weakly bound, linearly adsorbed CO species. This can be due to a decrease in metal crystallite size or also to a metal-support interaction which might result either in electron transfer between the metal particles and the support or in the stabilization of surface structures not normally present on such large metal crystallites.

With Pt catalysts, crystallite size clearly seems to play the predominant role in determining specific activity for the methanation reaction. On the other hand, with Pd catalysts the support itself appears to be the major factor and the activity seems to depend on the acidity of the support chosen, i.e., the more acidic the support, the higher the specific activity in the methanation reaction. This trend is similar to that found by Figueras *et al.* (6,7) for benzene hydrogenation over a series of support Pd catalysts. The turnover number increased by a factor of 4 as the acidity of the support increased. Taylor *et al.* (4) and Yates *et al.* (5) observed an opposite trend using supported Ni and Co catalysts for

ethane hydrogenolysis. In this reaction, an increase in support acidity decreased the specific activity. However, this behavior is consistent with the postulate of Figueras *et al.* (7) and Dalla Betta and Boudart (21) that electron transfer occurs from the metal to the support thereby depleting the free electron concentration of the metal particles. Using a simplistic argument, if this occurred with the catalysts studied in ethane hydrogenolysis, Ni would take on an electronic character more similar to Co, and Co would acquire electronic properties more similar to Fe. In each case a decrease in activity would be expected since Sinfelt (2) has shown that the specific activities for hydrogenolysis decrease in the order Ni > Co > Fe.

Although the alteration of the catalytic properties of 10 nm metal particles by electron transfer to the support is not easy to visualize, the behavior of Pd is consistent with this hypothesis. If such an effect exists, the catalytic activity of Pd might be expected to shift toward that measured for the metals immediately to the left of Pd in the periodic table. Since both Rh and Ru possess a higher specific activity (9), such a metal-support effect would enhance the activity of Pd which is in agreement with experimental results. However, it should be mentioned that a clear-cut choice cannot be made between this explanation and that postulating epitaxial stabilization of specific crystalline planes which favor the formation of weakly adsorbed CO. Regardless, despite its origin, the enhancement of the more weakly bound CO species seems clearly associated with the increase in specific activity.

### CONCLUSION

The results from this study provide evidence that the support itself can alter the catalytic activity of the metal component dispersed on its surface. This effect may be indirect, as in the case of Pt, where the primary role of the support is to produce stable, highly dispersed Pt clusters which

have a higher specific activity than very large Pt crystallites. However, a direct metal-support interaction, quite possibly involving electron transfer, appears to exist with Pd catalysts that is relatively independent of metal particle size, at least when the Pd crystallites are ca. 100 Å or less. In this case the nature of the support itself, rather than variations in metal particle size, produces the greatest change in specific activity. In either case, though, the net result is an increase in the more weakly bound adsorbed CO species which would be expected to enhance the rate of methanation (10). These results are consistent with the model suggested by Figueras *et al.* (7) for Pd catalysts and that proposed by Dalla Betta and Boudart (21) for Pt/zeolite catalysts, each of which assumes a depletion of the electron concentration in the metal particles due to transfer to the support. Direct verification of this assumption of electron transfer between the metal and the support must await the application of appropriate physical techniques to these catalyst systems.

#### ACKNOWLEDGMENT

The author thanks Donna Piano who performed most of the experimental work in this study.

#### REFERENCES

1. Boudart, M., in "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.
2. Sinfelt, J. H., *Cat. Rev.* **3**, 175 (1969).
3. Slinkin, A. A., and Fedorovskaya, E. A., *Russ. Chem. Rev.* **40**, 860 (1971).
4. Taylor, W. F., Yates, D. J. C., and Sinfelt, J. H., *J. Phys. Chem.* **68**, 2962 (1964).
5. Yates, D. J. C., Sinfelt, J. H., and Taylor, W. F., *Trans. Faraday Soc.* **61**, 2044 (1965).
6. Romero, R. G., and Figueras, F., *C. R. Acad. Sci.* **275**, 769 (1972).
7. Figueras, F., Gomez, R., and Primet, M., *Advan. Chem. Ser.* **121**, 480 (1973).
8. Figueras, F., Menciaer, B., DeMourgues, L., Nacache, C., and Trambouze, Y., *J. Catal.* **19**, 315 (1970).
9. Vannice, M. A., *J. Catal.* **37**, 449 (1975).
10. Vannice, M. A., *J. Catal.* **37**, 462 (1975).
11. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 705 (1965).
12. Koros, R. M., and Nowak, E. J., *Chem. Eng. Sci.* **22**, 470 (1967).
13. Schlatter, J. C., and Boudart, M., *J. Catal.* **24**, 282 (1972).
14. Freel, J., *J. Catal.* **25**, 139 (1972); *J. Catal.* **25**, 149 (1972).
15. Darensbourg, D. J., and Eischens, R. P., *Proc. Int. Congr. Catal.*, **5th**, 1972 **1**, 21-371 (1973).
16. Kikuchi, E., Flynn, P. C., and Wanke, S. E., *J. Catal.* **34**, 132 (1974).
17. Poltorak, O. M., and Boronin, V. S., *J. Phys. Chem. (USSR)* **39**, 1329 (1965).
18. Van Hardeveld, R., and Hartog, F., in "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 22, p. 75. Academic Press, New York, 1972.
19. Clarke, J. K. A., Farren, G., and Rubalcava, H. E., *J. Phys. Chem.* **71**, 2376 (1967).
20. Soma-Noto, Y., and Sachtler, W. M. H., *J. Catal.* **32**, 315 (1974).
21. Dalla Betta, R. A., and Boudart, M., in "Catalysis" (J. Hightower, Ed.), p. 1329. North-Holland, Amsterdam, 1973.