

STRONG METAL-SUPPORT INTERACTIONS

M. Albert Vannice
Department of Chemical Engineering
The Pennsylvania State University
University Park, PA 16802, USA

If bifunctional catalysts are discounted, i.e., metals dispersed on acidic oxides in which the metal provides hydrogenation-dehydrogenation activity and the oxide support induces carbonium ion chemistry (1), the number of well-documented examples of rate enhancement by the support is not large. One major reason for this is that the requirement of specific activities (molecules per second per unit metal surface area) or turnover frequencies (molecules per second per surface metal atom) was not fulfilled. It should be stressed at this time that observed changes in catalytic activity as the support is varied cannot automatically be attributed to metal-support interactions. First, artifacts created by heat and mass transfer limitations must be ruled out by conducting experiments at low conversions and using tests to verify the absence of these transport effects (2). Second, metal crystallite size effects must be ruled out. Third, in CO hydrogenation reactions in particular, chromatographic effects by the porous support must be eliminated. Finally, any influence of impurities, poisons and promoters must be eliminated, and the possibility of the support acting as a getter must be considered. In the absence of any direct spectroscopic evidence that a metal-support interaction exists, it is only after all other possibilities have been ruled out that the explanation of metal-support effects can safely be accepted.

Evidence that a dispersed phase on a substrate could have its catalytic behavior altered by that substrate was first reported by Schwab and co-workers (3-5) and Szabo and Solymosi (6,7); however, effects on specific activity of metals were not determined in these early studies. Later investigations by Sinfelt and co-workers provided some of the first evidence that the support could affect the specific activity of the dispersed metal (8), and the possibility of electronic interactions between the metal and the support was discussed in an early review (9). After this, Sagert and Pouteau showed that the degree of graphitization of the carbon support had a major effect on both the activation energy and the specific activity of the hydrogen-water deuterium exchange reaction over Pt (10,11).

However, it wasn't until the work of Tauster and co-workers that the effect of the support on chemisorption properties was observed (12,13), with titania, in particular, inhibiting the chemisorption of H_2 and CO on the Group VIII noble metals after high temperature reduction (HTR) at 773 K. A low temperature reduction (LTR) near 473 K provided normal chemisorption behavior. This behavior, which could be reversed by exposure to oxygen, was attributed to a Strong Metal-Support Interaction (SMSI). Catalytic studies of CO hydrogenation over TiO_2 -supported metals by Vannice and co-workers showed the specific activity, i.e., the turnover frequency (TOF), was markedly enhanced over many, but not all, of the Group VIII metals (14-21). In some systems, such as Ni/ TiO_2 , significant changes in selectivity to heavier paraffins were also found (14,16). Since these initial publications, many subsequent

investigations have been directed toward these catalytic systems, principally titania-supported metals, in an effort to better understand this phenomenon (22-67), and an international meeting was held on this topic in 1982 (68).

Perhaps the most apparent manifestation of "SMSI" behavior is the inhibition of H_2 and CO chemisorption on Group VIII noble metals dispersed on titania, as illustrated in Table 1, and certain other supports such as Ta_2O_5 , and Nb_2O_5 after high temperature reduction (HTR) at 773 K (10,11). Explanations such as sintering, contamination and encapsulation by the support were initially ruled out (12), and later CAEM (Controlled Atmosphere Electron Microscopy) studies by Baker et al. on Pt/substrate systems under UHV conditions provided further evidence that this behavior was a consequence of a metal-support interaction (33). This latter study was of particular interest because it showed: (1) morphological changes occurred for the Pt crystallites on titania and 2-dimensional "pill-box" structures were formed after HTR; (2) this change could be reversed by exposure to O_2 or H_2O to form thicker hemispherical particles, and (3) reduction of the TiO_2 to Ti_4O_7 , occurred and appeared to be closely associated with "SMSI" behavior. Interestingly, oxygen adsorption on TiO_2 -supported noble metals does not seem to be greatly affected (36) and may provide a useful chemisorption technique for these systems. This has been already proposed for Ni/ TiO_2 catalysts (22). Recent work by Baker and co-workers has provided additional evidence that a reduced phase of titania, again presumably Ti_4O_7 , is present when "SMSI" behavior exists (49). However recent studies have provided overwhelming evidence that the decrease in chemisorption capacity is principally due to the migration of TiO_x species onto the metal surface during the high temperature reduction step and that physical blockage of the surface metal atoms occurs (36,69).

Significant enhancements in specific activity have been found for CO hydrogenation over TiO_2 -supported Group VIII metals although not all metals are affected in a favorable manner (19). The much lower activity for iron may be a consequence of migration into the titania structure, as found by Tatarchuk and Dumesic (64-66). Titania-supported nickel catalysts are the most active reported to date for CO hydrogenation, as shown in Table 2, and the higher TOF values first reported by Vannice and co-workers (14-21) have subsequently been observed for Ni by other investigators (24,34,35,57). The high TOF values shown in Tables 3 and 4 for Pd and Pt, especially on Pt, are important because they vary by over two orders of magnitude even if the metal surface area is assumed equal to that existing after a LTR, which produces normal chemisorption behavior (18,21). Crystallite size effects were shown to be absent in both studies. However, significant changes in the adsorbed state of CO were detected by IR spectroscopy. Whereas H_2 has little effect on CO adsorbed on typical Pd and Pt catalysts, it significantly decreased the IR band intensities on the TiO_2 -supported metals, as shown in Figures 1 and 2 (20,58). Under steady-state reaction conditions, almost no IR-active CO existed on the TiO_2 -supported metals, in sharp contrast to the behavior of these metals dispersed on common supports, as shown by a comparison of Figures 1a and 1b and of Figures 2a and 2b. Additional examples are shown in Figure 3. Although there is common agreement that CO hydrogenation reaction rates are higher over most TiO_2 -supported metals (53,68), similar rate enhancements usually do not occur in other hydrogenation reactions and in hydrogenolysis reactions. In fact, after HTR to induce "SMSI" behavior, large decreases in activity have been observed for ethane hydrogenolysis (37,56), n-butane hydrogenolysis (36,70), benzene hydrogenation (36,71,72), n-hexane reactions (71) and cyclohexane dehydrogenation (36). Some of these results are reported

in Tables 5 and 6. Although normal activities for benzene hydrogenation, hexane reactions and ethane hydrogenolysis have been reported over Ni/TiO₂ catalysts (53,57,73), Pd/TiO₂ catalysts reduced at low temperature had enhanced benzene hydrogenation activity compared to typical Pd catalysts (72). A treatment in oxygen tends to restore the typical catalytic properties of these metals (36).

In addition to significant rate enhancements for CO hydrogenation, (and perhaps of greater importance) pronounced changes in selectivity can occur for some TiO₂-supported metals. The changes in Ni/TiO₂ catalysts to produce long-chain paraffins are quite vivid (14,16), as shown in Tables 7 and 8. Vannice and Garten also found that olefin formation was enhanced over TiO₂-supported Ru, compared to typical Ru catalysts (15), and Morris et al. later found similar behavior (74). Under certain reaction conditions, methane formation constituted less than 15 wt% of the hydrocarbon product (12-14).

The chemistry responsible for SMSI behavior is still not completely understood, especially since the occurrence of inhibited chemisorption does not always parallel an increase in catalytic activity (21,74). A number of explanations have been proposed for "SMSI" behavior, and they include: (1) changes in structure, i.e., formation of thin rafts; (2) intermetallic compound formation; (3) electron transfer to Pt via Ti³⁺ cations formed during reduction; (4) electron transfer to Pt from the Fermi level of bulk titania via a metal/semiconductor interface (i.e., a Schottky barrier); (5) titania migration onto the metal surface; and (6) increased, rather than weakened, metal-H bond strengths. To explain the higher activity for CO hydrogenation, additional proposals invoking special sites in the adlineation region, i.e., at the metal-support interface (53,69) and H₂ spillover during reaction have also been made. At the present time, little evidence has been found to support the notion of surface intermetallic compound formation in metal/titania systems (36) and, in actuality, bulk intermetallic compounds have been found to convert to metal/metal oxide systems under CO hydrogenation reaction conditions (75,76). Enhanced hydrogen adsorption, i.e., stronger H-metal bonding, has also been discounted (33).

The CAEM studies by Baker and co-workers on supported Pt and AgPt have clearly shown that the morphology of Pt crystallites changes on reduced titania, and they appear to wet the support surface by forming thin rafts, as depicted in Figure 4 (33,49). This structural change could have a effect on adsorption and catalytic properties even if no electron transfer occurred and, in addition, such wetting of the surface would also increase the metal-support interface and facilitate electron transfer as proposed in explanation 3 or 4. The Exxon workers have favored direct metal atom-support cation (Ti³⁺) interactions (32) - a more localized bonding model - whereas others have proposed electron transfer dependent upon electronic properties of the bulk oxide support via a Schottky barrier (28-30,36). Although behavior indicating electron transfer from the titania to the metals has in some cases been observed by using a variety of techniques such as XPS (23-27) and electrical conductivity measurements (28-30), as shown in Figures 5 and 6, such results have not always been obtained (38).

The ability of TiO₂-supported metals to selectively enhance the rate of CO hydrogenation, but not other hydrogenation or hydrogenolysis reactions, implies that the effect responsible has a strong influence on adsorbed CO. The two most likely possibilities are a structural effect due to electron transfer and particle morphological changes, or the creation of unique sites at the metal/support interface, or possibly a combination of the two

(21,53,69). This proposal of special active sites in the metal/support interface region, i.e., the theory of adlineation, is an old concept first proposed by Schwab⁽³⁾. The migration of TiO_2 onto the metal surface would tend to enhance this effect and also minimize any metal crystallite size effect governing interfacial area (21). Although special active sites for the CO molecule could play a role, an enhanced surface concentration of hydrogen under reaction conditions may also account for the much higher activities observed (18,21); however, recent studies have provided strong support for the creation of unique active sites at the metal-support interface, for instance, note the high turnover frequencies shown in Table 9 (69). The model resulting from this study is shown in Figure 7, and it invokes special sites at the metal-titania interface which interact with the oxygen end of the CO molecule to facilitate bond rupture, which is the slow step on Pt and Pd catalysts.

A model invoking special active sites on the titania surface which are outside the adlineation region, but participate in CO hydrogenation reactions via hydrogen spillover (i.e., surface migration), has not been supported by recent studies (63). Regardless, the role of spillover under reaction conditions is presently obscure. Under low temperature conditions with active hydrogenation catalysts, predicted rates of hydrogen transport on the support surface, using calculated surface diffusion coefficients, are too low to be significant compared to rates of reaction on the metal surface (77-79). In contrast, under typical reaction conditions for methanation over the less active metals (1 atm, 275°C, $\text{H}_2/\text{CO}=3$), calculated rates of hydrogen transfer to the support per metal crystallite can be comparable to rates of reaction per crystallite. For example, using the solution to the equation describing 2-dimensional surface diffusion (77), calculating a diffusion coefficient of $7 \times 10^{-18} \text{ cm}^2 \cdot \text{s}$ at 275°C from the work of Kramer and Andre (79), and assuming 1 nm Pt crystallites containing 20 Pt atoms with a hydrogen coverage of $\Theta_{\text{H}}=0.1$, a maximum transport rate to the support of 0.03 H atoms per second per crystallite can be estimated. The rate of H consumption during methanation on Pt/ Al_2O_3 catalysts is 0.13 H atoms per second per Pt crystallite (21). This comparison is made to show that although hydrogen spillover does not seem to be adequate to explain the higher turnover frequencies found on TiO_2 -supported metals, if comparable diffusion coefficients are assumed, this process could enhance the rate in the adlineation region because this transport process involves only a very short jump distance. Despite this exercise to ascertain the possible contribution of H_2 spillover to reaction rates, its actual role has not yet been determined. Although hydrogen spillover alone does not appear to provide an explanation for enhanced CO hydrogenation activity, it is clearly important in facilitating "SMSI" behavior by catalyzing the reduction of TiO_2 (25,33,49,80). The reduction of other metal oxides at lower than normal temperatures via hydrogen spillover from a metal capable of activating H_2 has also been reported (81-94).

At the present time there is much interest in metal-support effects, particularly with regard to their role in CO hydrogenation reactions. The chemistry inducing "SMSI" behavior and activity enhancement is still not yet completely resolved and future studies are needed to determine: (1) the extent of electron transfer between metal and support, should it occur; (2) whether this is localized behavior at the surface or best described by metal/semiconductor bulk properties; (3) the effect of structural (morphological) changes in the metal crystallites; (4) the contribution of the adlineation region to the catalytic process; (5) the importance, if any, of hydrogen spillover in the catalysis of CO hydrogenation reactions; and (6)

whether metal-support effects occur in other reactions involving CO, such as oxidation.

In view of the interest in CO oxidation, a short comment pertaining to crystallite size effects seems appropriate. Recent studies of integral heats of adsorption on Pd catalysts have shown that Q_{ad} values for CO and O₂ increase markedly on crystallites smaller than 3 nm, as shown in Figures 8 and 9 (95-97). Such a large change has not been observed for supported Pt catalysts, but the support has a significant influence on CO heats of adsorption (98). Such changes in heats of adsorption can have a large effect on the kinetics of reactions involving these species; consequently, it seems important to study the influence of these parameters on CO oxidation over noble metals like Pt and Pd.

In summary, it has now been unambiguously demonstrated that synergistic metal-support effects can occur which markedly enhance specific activity and alter selectivity in certain reactions. Because of the presence of such effects in certain reactions conducted under reducing conditions (that is, under H₂ pressure), but not others, the creation of unique sites at the metal-support interface seems to be the best model at the present time to explain this behavior. The postulation of these sites, which are specific for a certain reactant such as CO, provides an effective explanation for the higher methanation rates that have been reported over some catalysts. The creation of these sites in the adlineation zone is facilitated by hydrogen spillover from the metal surface, and this same process can also enhance the reduction of many oxide supports. Although oxygen spillover is much less probable due to its higher heat of adsorption, it is much less well understood and the possibility of rate enhancements in CO oxidation caused by special interface sites cannot be discounted at the present time. Consequently, this seems to be an important area of research in the future.

REFERENCES

1. Sinfelt, J. H., Adv. Chem. Eng. 5, 37 (1964).
2. Madon, R. J. and Boudart, M., I&EC Fund. 21, 438 (1982).
3. Schwab, G-M., Adv. Catal. 27, 1 (1978).
4. Schwab, G-M., Block, J., Muller, W. and Schultze, D., Naturwiss, 44, 582 (1957).
5. Schwab, G-M., Block, J. and Schultze, D., Angew. Chem. 17, 101 (1959).
6. Szabo, Z. G. and Solymosi, F., Act. Deux. Cong. Inter. Catalyse, Paris 1627 (1961).
7. Solymosi, F., Cat. Rev. 1, 233 (1967).
8. Sinfelt, J., Cat. Rev. 3, 175 (1969).
9. Slinkin, A. A. and Fedorovskaya, E. A., Russ. Chem. Rev. 40, 860 (1971).
10. Sagert, N. H. and Pouteau, R. M. L., Can. J. Chem. 50, 3686 (1972).
11. Sagert, N. H. and Pouteau, R. M. L., Pt Metals Rev. 19, 16 (1975).
12. Tauster, S. J., Fung, S. C. and Garten, R. L., J. Am. Chem. Soc. 100, 170 (1978).
13. Tauster, S. J. and Fung, S. C., J. Catal. 55, 29 (1978).
14. Vannice, M. A. and Garten, R. L., J. Catal. 56 236 (1979).
15. Vannice, M. A. and Garten, R. L., J. Catal. 63, 255 (1980).
16. Vannice, M. A. and Garten, R. L., J. Catal. 66, 242 (1980).
17. Vannice, M. A., Moon, S. H. and Twu, C. C., ACS Prepr.-Petr. Chem. Div. 25, 303 (1980).
18. Wang, S-Y., Moon, S. H. and Vannice, M. A., J. Catal. 71, 167 (1981).
19. Vannice, M. A., J. Catal. 74, 199 (1982).
20. Vannice, M. A., Twu, C. C. and Moon, S. H., J. Catal. 79, 70 (1983).
21. Vannice, M. A. and Twu, C. C., J. Catal. 82, 213 (1983).
22. Smith, J. S., Thrower, P. A. and Vannice, M. A., J. Catal. 68, 270 (1981).
23. a) Bahl, M. K., Tsai, S. C., Chung, Y. W., Phys. Rev. B21, 1344 (1980).
 b) Kao, C. C., Tsai, S. C., Bahl, M. K., Chung, Y-W. and Lo, W. J., Surf. Sci. 95, 1 (1980).

24. Kao, C-C., Tsai, S-C. and Chung, Y-W., J. Catal. 73, 136 (1982).
25. Sexton, B. A., Hughes, A. E. and Fogar, K., J. Catal. 77, 85 (1982).
26. Chien, S. H., Shelimov, B. N., Resasco, D. E., Lee, E. H. and Haller, G. L., J. Catal. 77, 301 (1982).
27. Fung, S. C., J. Catal. 76, 225 (1982).
28. Chen, B-H. and White, J. M., J. Phys. Chem. 86, 3534 (1982).
29. Herrmann, J-M. and Pichat, P., J. Catal. 78, 425 (1982).
30. Disdier, J., Herrmann, J-M. and Pichat, P., JCS Faraday I 79, 651 (1983).
31. Horsley, J. A., J. Am. Chem. Soc. 101, 2870 (1979).
32. Tauster, S. J., Fung, S. C., Baker, R. T. K. and Horsley, J. A., Science 211, 1121 (1981).
33. a) Baker, R. T. K., Prestridge, E. B. and Garten, R. L., J. Catal. 56, 390 (1979);
b) Ibid. 59, 293 (1979).
34. Bartholomew, C. H. and Mustard, D. G., J. Catal. 67, 186 (1981).
35. Bartholomew, C. H., Pannell, R. B., Butler, J. L. and Mustard, D. G., I&EC Prod. Res. Dev. 20, 296 (1981).
36. Meriaudeau, P., Ellestad, O. H., Dufaux, M. and Naccache, C., J. Catal. 75, 243 (1982).
37. Ko, E. I. and Garten, R. L., J. Catal. 68, 233 (1981).
38. Huizinga, T. and Prins, R., J. Phys. Chem. 85, 2156 (1981).
39. Huizinga, T. and Prins, R., J. Phys. Chem. 87, 173 (1983).
40. Ko, E. I., Winston, S. and Woo, C., JCS Chem. Comm. 740 (1982).
41. Mochida, I., Tsuji, K., Suetsugu, K., Fujitsu, H. and Takeshita, K., J. Phys. Chem. 84, 3159 (1980).
42. Praliand, H. and Martin, G. A., J. Catal. 72, 394 (1981).
43. Tsai, W., Schwarz, J. A. and Driscoll, C. T., J. Phys. Chem. 87 1619 (1983).
44. Summers, J. C. and Ausen, S. A., J. Catal. 58, 131 (1979).
45. Chen, B-H., White, J. M., Brostrom, L. R. and Deviney, M. L., J. Phys. Chem. 87, 2423 (1983).
46. White, J. M. and Tanaka, K., J. Phys. Chem. 86, 3977 (1982).

47. Tanaka, K. and White, J. M., J. Catal. 79, 81 (1983).
48. DeCanio, S. J., Apple, T. M. and Dybowski, C. R., J. Phys. Chem. 87, 194 (1983).
49. Baker, R. T. K., Prestridge, E. B. and Murrell, L. L., J. Catal. 79, 348 (1983).
50. Bossi, A., Garbassi, F., Petrini, G., Zanderighi, L., JCS Faraday Tr I 78, 1029 (1982).
51. Brenner, A. and Hucal, D. A., J. Phys. Chem. 85, 496 (1981).
52. Briggs, D., Dewing, J., Burden, A. G., Moyes, R. B. and Wells, P. B., J. Catal. 65, 31 (1980).
53. Burch, R. and Flambard, A. R., J. Catal. 78 389 (1982).
54. Gonzales, A. R., Soria, J. and Munuera, G., J. Catal. 76, 254 (1982).
55. Haller, G. L. and Resasco, D., JCS Chem. Comm. 1150 (1980).
56. Haller, G. L., Resasco, D. E. and Rouco, A. J., Faraday Disc. 72, (7) (1981).
57. Burch, R. and Flambard, A. R., JCS Chem. Comm. 123 (1981).
58. Vannice, M. A., Wang, S-Y. and Moon, S. H., J. Catal. 71, 152 (1981).
59. Vannice, M. A. and Wang, S-Y., J. Phys. Chem. 85, 2543 (1981).
60. Vannice, M. A. and Twu, C. C., J. Chem. Phys. 75, 5944 (1981).
61. Apple, T. M., Gajardo, P. and Dybowski, C., J. Catal. 68, 103 (1981).
62. Conesa, J. C. and Soria, J., J. Phys. Chem. 86, 1392 (1982).
63. Vannice, M. A. and Vasco-Jara, J., Studies in Surface Science and Catalysis, Vol. 11, B. Imelik et al., Eds., Elsevier, p. 185 (1982).
64. Tatarchuk, B. J. and Dumesic, J. A., J. Catal. 70, 308 (1981).
65. Tatarchuk, B. J. and Dumesic, J. A., J. Catal. 70, 323 (1981).
66. Tatarchuk, B. J. and Dumesic, J. A., J. Catal. 70, 335 (1971).
67. Tatarchuk, B. J., Chludzinski, J. J., Sherwood, R. D., Dumesic, J. A. and Baker, R. T. K., J. Catal. 70, 443 (1981).
68. Studies in Surface Science and Catalysis, Vol. 11, "Metal-Support and Metal-Additive Effects in Catalysis," B. Imelik et al., Eds., Elsevier, 1982.
69. Vannice, M. A. and Sudhaker, C., J. Phys. Chem. 88, 2429 (1984), and reference therein.

70. Resasco, D. E. and Haller, G. L., Ref. 68, p. 105.
71. Meriadeau, P., Dutel, J. F., Dufaux, M. and Naccache, C., Ref. 68, p. 95.
72. Vannice, M. A. and Chou, P., Proc 8th Inter. Cong. on Catal. V-99, DEHEMA, Frankfurt, 1984.
73. Burch, R. and Flambard, A. R., Ref. 68, p. 193.
74. Morris, S. R., Moyes, R. B., Wells, P. B. and Whyman, R., Ref. 68, p. 247.
75. Imamura, H. and Wallace, W. E., J. Catal. 65, 127 (1980).
76. Chin, R. L., Elattar, A., Wallace, W. E. and Hercules, D. M., J. Phys. Chem. 84, 2895 (1980).
77. Vannice, M. A. and Neikam, W. C., J. Catal. 27, 207 (1972).
78. Fleisch, T. and Abermann, R., J. Catal. 50, 268 (1977).
79. Kramer, R. and Andre, M., J. Catal. 58, 287 (1979).
80. Vannice, M. A., Odier, P., Bujor, M. and Fripiat, J. J., ACS Symp. Series 228, 98 (1985).
81. Boudart, M., Vannice, M. A. and Benson, J. E., Z. physik. Chem. NF 64, 171 (1969).
82. Vannice, M. A., Boudart, M. and Fripiat, J. J., J. Catal. 17, 359 (1970).
83. Levy, R. B. and Boudart, M., J. Catal. 32, 304 (1974).
84. Bolivar, C., Charcosset, H., Frety, R., Primet, M., Tournayan, L., Betizeau, C., Leclercq, G. and Maurel, R., J. Catal. 39, 249 (1975).
85. Bond, G. C. and Tripathi, J. B. P., JCS Faraday I 72, 933 (1976).
86. Ekstrom, A., Batley, G. E. and Johnson, D. A., J. Catal. 34, 106 (1974).
87. Frety, R., Charcosset, H. and Trambouze, Y., Ind. Chim. Belg. 38, 501 (1973).
88. Erre, R., Van Damme, H. and Fripiat, J. J., Surf. Sci. 127, 48 (1983).
89. Erre, R., Legay, M. H. and Fripiat, J. J., Surf. Sci. 127, 69 (1983).
90. Gentry, S. J., Hurst, N. W. and Jones, A., JCS Faraday I, 77, 603 (1981).
91. Sancier, K. M., J. Catal. 23, 298 (1971).
92. Viswanath, R. P., Viswanathan, B. and Sastri, M. V. C., React. Kin. Catal. Lett. 2, 51 (1975).

93. Nowak, E. J. and Koros, R. M., J. Catal. 7, 50 (1967).
94. Nowak, E. J., J. Phys. Chem. 73, 3790 (1969).
95. Vannice, M. A. and Chou, P., ACS Symp. Ser. 298, 76 (1986).
96. Chou, P. and Vannice, M. A., Calorimetric Heat of Adsorption Measurements on Palladium. Part 2. Influences of Crystallite Size and Support on CO Adsorption., J. of Catal, 1987.
97. Chou, P. and Vannice, M. A., Calorimetric Heat of Adsorption Measurements on Palladium. Part 3. Influences of Crystallite Size and Support on O₂ Adsorption., J. of Catal, 1987.
98. Sen B., Chou, P. and Vannice, M. A., J. Catal., vol. 101, p. 517, 1986.

TABLE 1

(From Ref. 12) *

Hydrogen and CO Sorption at $25 \pm 2^\circ\text{C}$ on TiO_2 -Supported Metals

Metal	Redn temp, $^\circ\text{C}$	H/M, $\mu\text{mol/g}$	CO/M, $\mu\text{mol/g}$	BET area, $\text{m}^2 \text{g}^{-1}$
2% Ru	200	0.23	0.64	45
	500	0.06	0.11	46
2% Rh	200	0.71	1.15	48
	500	0.01	0.02	43
2% Pd	175	0.93	0.53	42
	500	0.05	0.02	46
2% Os	200	0.21		
	500	0.11		
2% Ir	200	1.60	1.19	48
	500	0.00	0.0	45
2% Pt	200	0.88	0.65	
	500	0.00	0.03	
Blank TiO_2	150 ^a	b		51
Support	500	b		43

^a Evacuated for 2 h at 150°C ; no reduction prior to BET area determination. ^b H_2 uptake on these samples exhibited Henry's law behavior and was zero at $P_{\text{H}_2} = 0$ by extrapolation.

*Reprinted with permission, copyright ©, 1978, American Chemical Society.

TABLE 2

(From Ref. 14) *

Specific Activities of Ni/TiO_2 Relative to Other Ni Catalysts for the CO-H_2 Reaction^a

Catalyst	N_{CO} ($\text{sec}^{-1} \times 10^3$)		N_{CH_4} ($\text{sec}^{-1} \times 10^3$)	
	H_2 (fresh)	H_2 (used)	H_2 (fresh)	H_2 (used)
1.5% Ni/TiO_2	500		231	528
1.5% Ni/TiO_2 (100) ^b		16		7.4
10% Ni/TiO_2	1607		196	305
10% Ni/TiO_2 (100) ^b		90		11
5% $\text{Ni}/\eta\text{-Al}_2\text{O}_3$	19.6	44	16.4	37
8.8% $\text{Ni}/\eta\text{-Al}_2\text{O}_3$	10.7	128	7	85
42% $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$	58	109	23.8	43
30% $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$	32.3	35	16.6	18
16.7% Ni/SiO_2	14.8	47	10.7	34
20% Ni/graphite	43.1	79	27.8	51
Ni powder	30	18	26.6	16

^a Reaction conditions: 548°K (275°C), 103 kPa (1 atm), $\text{H}_2/\text{CO} = 3$.

^b Calculated assuming 100% nickel metal exposed.

*Copyright ©, 1979, by Academic Press, Inc.

TABLE 3
(From Ref. 18)*

Kinetic Properties of Palladium Catalysts^a

Catalyst	Rate ($\mu\text{mole CH}_4/\text{s} \cdot \text{g cat.}$)	$N_{\text{CH}_4} (\text{s}^{-1} \times 10^3)$		E_a (kcal mol^{-1})	Average particle size ^c (nm)
		(b)	(c)		
1.98% Pd/ $\eta\text{-Al}_2\text{O}_3$ (C)	0.200	4.6	3.0	13.8 ± 0.6	3.2
(F) 2% Pd/ Al_2O_3 ^d	—	12	—	19.7 ± 1.6	4.8 ^e
(G) 2% Pd/ $\eta\text{-Al}_2\text{O}_3$ ^f	0.125	3.1	3.2	19.2 ± 0.8	5.4
1.98% Pd/ $\eta\text{-Al}_2\text{O}_3$	0.108	4.8	2.8	19.7 ± 1.3	5.7
(G) 2% Pd/ Al_2O_3 ^d	—	7.4	—	23.6 ± 1.9	8.2 ^e
1.79% Pd/ $\eta\text{-Al}_2\text{O}_3$	0.109	8.8	5.9	19.4 ± 0.7	10.2
(H) 9.5% Pd/ Al_2O_3 ^d	—	7.4	—	21.0 ± 0.8	12.0 ^e
(H) 9.5% Pd/ $\eta\text{-Al}_2\text{O}_3$ ^f	0.257	3.2	4.0	24.5 ± 1.1	15.7
10.28% Pd/ Al_2O_3 (S)	0.25	8.5	4.7	19.0 ± 1.0	20.0
10.28% Pd/ Al_2O_3 (C, S)	0.09	5.1	2.2	22.8 ± 0.6	26.3
2.12% Pd/ $\text{SiO}_2\text{-Al}_2\text{O}_3$	0.11	4.1	3.4	19.9 ± 0.3	7.0
(J) 4.75% Pd/ SiO_2 ^d	—	0.32	0.23	26.9 ± 1.8	3.1 ^e
(K) 4.75% Pd/ SiO_2 ^d	—	0.26	—	—	4.9 ^e
1.93% Pd/ SiO_2	0.0013	0.12	0.11	27.7 ± 2.6	18.0
8.78% Pd/ SiO_2 (C, S)	0.00103	1.0	0.34	19.2 ± 1.8	153
1.86% Pd/ TiO_2 (448 K) Sample 1	0.168	4.1 ^g	5.2 ^h	19.7 ± 1.2	6.2 ^e
Sample 2	0.187	4.5 ^g	5.8 ^h	22.4 ± 0.6	—
1.86% Pd/ TiO_2 (SMSI) Sample 1	0.128	18	32	24.3 ± 1.9	—
		3.1 ^g	4.0 ^h		
Sample 2	0.187	27	47	23.6 ± 0.7	—
		4.6 ^g	5.8 ^h		

^a $T = 548 \text{ K}$, $P_T = 1 \text{ atm}$, $\text{H}_2/\text{CO} = 3$.

^b Based on $\text{CO}_{(\text{red})}$ on used sample.

^c Based on $\text{H}_{(\text{red})}$ on used sample.

^d Results previously reported in Reference (4).

^e Based on $\text{CO}_{(\text{red})}$ on used sample assuming $\text{CO}/\text{Pd}_0 = 0.5$.

^f Results obtained in this study with fresh catalysts so designated in Reference 4.

^g Based on $\text{CO}_{(\text{red})}$ on fresh, reduced sample.

^h Based on $\text{H}_{(\text{red})}$ on fresh, reduced sample.

*Copyright ©, 1981, by Academic Press, Inc.

TABLE 4
(From Ref. 21)*

Kinetic Behavior of Platinum Catalysts^a

Catalyst ^b	Rate ($\frac{\mu\text{mole CH}_4}{\text{s} \cdot \text{g cat}}$)	$N_{\text{CH}_4}(\text{s}^{-1} \times 10^3)$		E_a (kcal mole ⁻¹)	Diameter (nm) (c)	CO conversion range (%)
		(c)	(d)			
$\gamma\text{-Al}_2\text{O}_3$						
1.75% Pt ^b		1.7		16.7	1.2	
A—2.1%						
I	0.134	1.7	3.5	16.2 ± 0.7	1.6	1.0–3.8
II	0.164	2.1	4.3	—	1.6	0.2–1.0
B—2.0%	0.040	1.6 ^c	2.4 ^c	16.5 ± 1.2	4.7 ^c	0.2–1.0
E—10.0%	0.092	1.4	2.4	16.7 ± 1.0	8.7	0.3–1.3
D—2.0%	—	—	—	—	38	—
C—2.0%	0.0024	1.7	2.3	17.6 ± 0.8	80	0.03–1.0
F—10.0%	0.0028	0.73	1.0	18.6 ± 1.4	160	0.05–0.2
$\gamma\text{-SiO}_2$						
J—2%	0.0084	0.14	0.31	—	1.9	<0.01
H—1.3%	0.0024	0.17	0.19	—	5.4	0.01–0.03
I—2%	0.0040	0.19	0.24	—	5.6	<0.01
G—1.5%	0.0016	0.19	0.19	16.8 ± 1.1	10	0.01–0.05
$\gamma\text{-SiO}_2\text{-Al}_2\text{O}_3$						
K—1.5%	0.029	1.4	1.6	16.4 ± 1.0	4.2	0.2–1.0
$\gamma\text{-TiO}_2$						
N—1.9% (LT)						
I	0.538	10.9	19	19.1 ± 0.6	2.2	2.6–16
II	0.737	14.9	26	20.3 ± 0.3	2.2	1.8–5.0
L—1.9% (LT)						
I	0.064	6.7	9.6	17.2 ± 0.7	11	0.4–1.8
II	0.081	8.4	12	19.0 ± 1.5	11	0.3–1.7
M—1.9% (LT)	0.084	14.5	29	—	19	—
P—1.9% (SMSI)						
I	0.564	59(11.3) ^f	120	20.6 ± 0.8	(2.2)	3.0–15
II	0.659	66(12.7) ^f	130	19.1 ± 1.6		0.7–4.2
O—1.9% (SMSI)						
I	0.150	54(16) ^e	110	17.7 ± 0.8	(11)	1.8–5.0
II	0.355	127(38) ^e	250	23.3 ± 3.2		0.8–4.9

^a $T = 548.2 \text{ K}$, $P_T = 101 \text{ kPa}$, $\text{H}_2/\text{CO} = 3$.

^b Roman numerals indicate different samples.

^c Based on final $\text{H}_{(\text{ad})}$.

^d Based on final $\text{CO}_{(\text{ad})}$.

^e Based on initial $\text{H}_{(\text{ad})}$.

^f Based on final $\text{H}_{(\text{ad})}$ on catalyst N.

^g Based on final $\text{H}_{(\text{ad})}$ on catalyst L.

^h From Ref. 8.

*Copyright ©, 1983, by Academic Press, Inc.

TABLE 5

USE OF TiO_2 AS A SUPPORT REDUCED ETHANE HYDROGENOLYSIS ACTIVITY OVER METALS

(From Ref. 37)*

Specific Activities^a for Ethane Hydrogenolysis at 205°C

Metal	SiO_2 -supported ^b	TiO_2 -supported ^c
Fe	1.2×10^{-5}	$< 10^{-13}$
Co	3.4×10^{-5}	1.0×10^{-9}
Ni	8.0×10^{-4}	8.0×10^{-7}
Ru	1.8×10^{-3}	1.4×10^{-3}
Rh	2.2×10^{-4}	2.9×10^{-3}
Pd	6.7×10^{-10}	2.6×10^{-13}
Os	4.2×10^{-2}	9.6×10^{-4}
Ir	1.1×10^{-4}	3.0×10^{-7}
Pt	7.2×10^{-10}	$< 10^{-13}$

^a Expressed in units of moles of ethane converted/hr/m².^b Calculated from Ref. (4).^c Calculated from Table 1.

*Copyright ©, 1981, by Academic Press, Inc.

TABLE 6

THE SMSI STATE DECREASES ACTIVITY FOR CERTAIN REACTIONS

(From Ref. 36)*

CATALYST	TREATMENT (TEMP. IN °K)	RATE (MMOL·H ⁻¹ ·G METAL ⁻¹)	
		C_6H_6 HYDROGENATION AT 288 K	C_6H_{12} DEHYDROGENATION AT 523 K
4.8 Pt/TiO ₂	H ₂ -523	40	1740
	H ₂ -523, O ₂ -273	56	----
	H ₂ -773	3.5	217
	H ₂ -773, O ₂ -273	29	1087
2.7% Ir/TiO ₂	H ₂ -523	81	1400
	H ₂ -523, O ₂ -273	159	----
	H ₂ -773	0	304
	H ₂ -773, O ₂ -273	18.5	----

*Copyright ©, 1982, by Academic Press, Inc.

TABLE 7

(From Ref. 14)*

Comparison of the Selectivity of Ni/TiO₂ to Other Ni Catalysts for the CO-H₂ Reaction

Catalyst	Reaction T (°K)	CO conversion (%)	mole% paraffin of each carbon number				
			C ₁	C ₂	C ₃	C ₄	C ₄₊
1.5% Ni/TiO ₂	524	13.3	58	14	12	8	7
10% Ni/TiO ₂	516	24	50	9	25	8	9
5% Ni/η-Al ₂ O ₃	527	10.8	90	7	3	1	—
8.8% Ni/η-Al ₂ O ₃	503	3.1	81	14	3	2	—
42% Ni/α-Al ₂ O ₃	509	2.1	76	1	5	3	1
16.7% Ni/SiO ₂	493	3.3	92	5	3	1	—
20% Ni/graphite	507	24.8	87	7	4	1	—
Ni powder	525	7.9	94	6	—	—	—

*Copyright ©, 1979, by Academic Press, Inc.

TABLE 8

(From Ref. 16)*

Comparison of 10% Ni/COT and 10% Ni/P-25*

Catalyst	CO conversion (%)	Product distribution (mole%)						
		C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇₊
10% Ni/COT	4.6	51.3	14.7	7.7	10.5	8.6	4.9	2.3
10% Ni/P-25	5.5	42.5	13.3	10.9	8.8	10.3	8.0	6.2

* T = 200°C, H₂/CO = 3, P = 101 kPa.

*Copyright ©, 1980, by Academic Press, Inc.

TABLE 9
(From Ref. 69)*

Effect of Titanium Oxide Deposited on Pt Surface								
catalyst ^a	T _R , °C	BET surface area, m ² g ⁻¹	irreversible adsorption, mol/g		TOF, ^b s ⁻¹ × 10 ³		E _a , kcal/mol	
			H ₂	CO	CH ₄	CO ₂	CH ₄	CO ₂
Pt powder								
initial	500	0.5	2.6	4.0				
final	500	0.4	2.5	3.5	0.11	0.008	16	27
TiO ₂ /Pt (monolayer)								
initial	500		1.7	3.3				
final	500		1.7	3.1	0.41	0.12	25	38
TiO ₂ /Pt (multilayer)								
initial	200		1.4	0.9	18	11	22	31
final	500	0.9	0.9	1.6	4.2	2.6	23	29
1.5% Pt/SiO ₂	450		4.1	8.0	0.17 ^c		16.8	
1.9% Pt/TiO ₂	200		24.7	28.0	13 ^c		19.7 ^c	
1.9% Pt/TiO ₂	500		4.8	4.8	63 ^c (12) ^d		20 ^c	

^a Final state is after completion of kinetic study. ^b Measured at 548 K, 100 kPa, H₂/CO = 3, based on H adsorbed on used sample. ^c Average values from ref 6. ^d Based on Pt₂ measured after 200 °C reduction.

*Reprinted with permission, copyright ©, 1984, American Chemical Society.

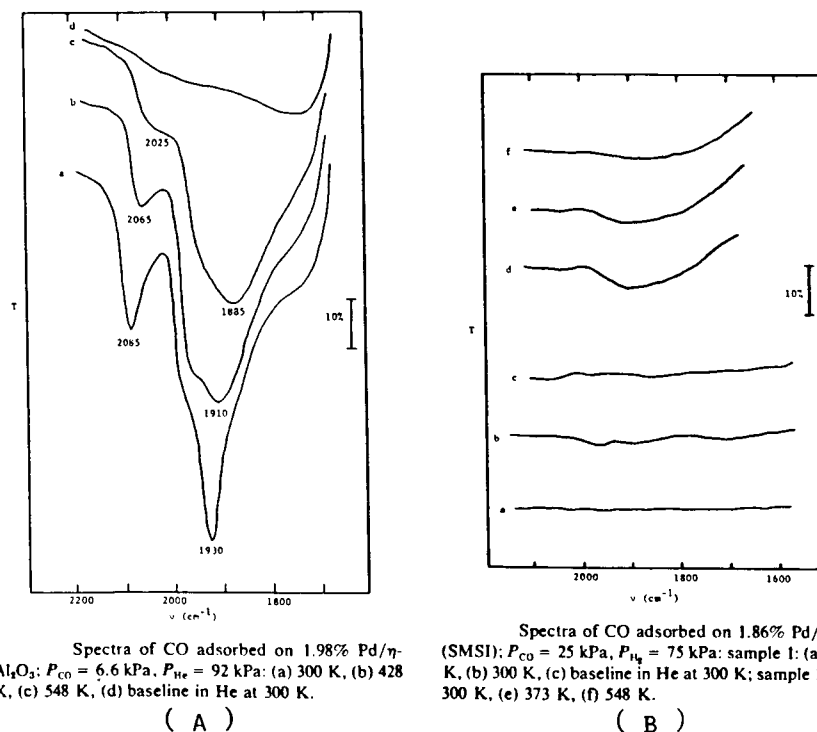
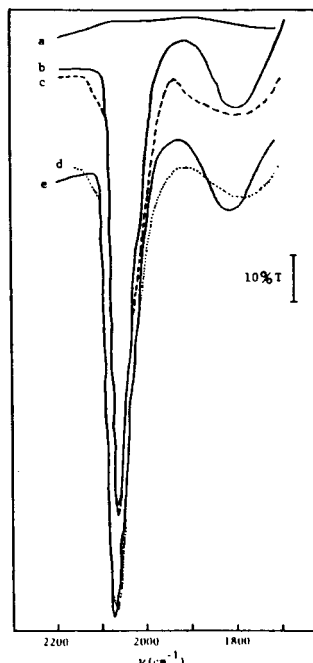


Figure 1. (From reference 18)*

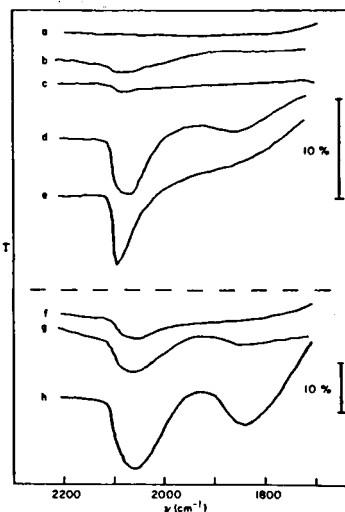
*Copyright ©, 1981, by Academic Press, Inc.

ORIGINAL PAGE IS
OF POOR QUALITY



Infrared spectra of CO adsorbed on 1.5% Pt/
SiO₂-Al₂O₃ ($P_{CO} = 185$ Torr, He/CO or H₂/CO = 3): (a)
baseline in He, (b) 3000 K in H₂, (c) 548 K in H₂, (d)
548 K in He, (e) 300 K in He.

(A)

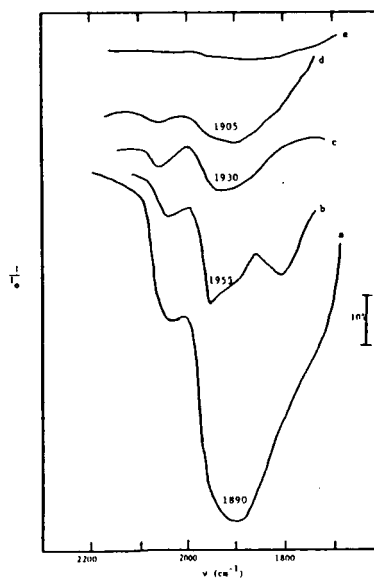


Infrared spectra of CO adsorbed on 1.9% Pt/
TiO₂ ($P_{CO} = 185$ Torr, He/CO or H₂/CO = 3): Catalyst
O (SMSI)—(a) baseline in He at 300 K, (b) 300 K in H₂,
(c) 548 K in H₂, (d) 300 K in He, (e) 548 K in He;
Catalyst N (LT)—(f) 473 K in H₂, (g) 300 K in H₂, (h)
300 K in He. Note change in transmittance scale.

(B)

Figure 2. (From reference 20)*

*Copyright ©, 1983, by Academic Press, Inc.



Relative intensities of CO adsorbed under
reaction conditions: $P_{Total} = 1$ atm, H₂/CO = 3, $T =$
548 K. I_0 is the baseline intensity in pure H₂ at 548 K.
(a) 1.98% Pd/ η -Al₂O₃, (b) 1.93% Pd/SiO₂, (c) 2.12%
Pd/SiO₂-Al₂O₃, (d) 1.86% Pd/TiO₂ (448 K), (e) 1.86%
Pd/TiO₂ (SMSI).

Figure 3. (From reference 18)*

*Copyright ©, 1981, by Academic Press, Inc.

PT CAN UNDERGO REVERSIBLE MORPHOLOGICAL CHANGES ON TITANIA

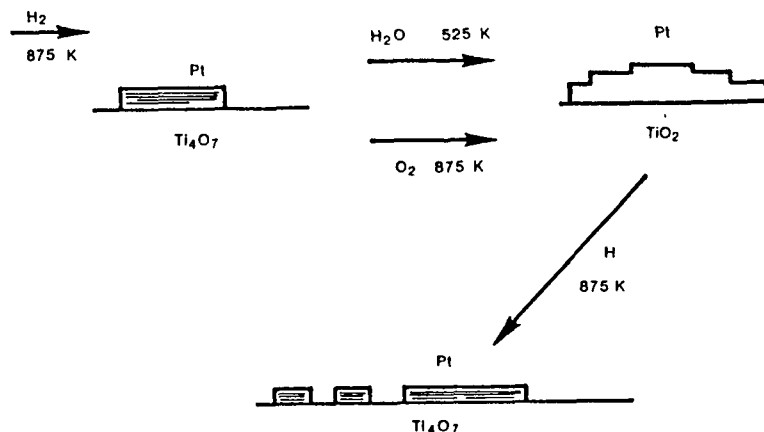
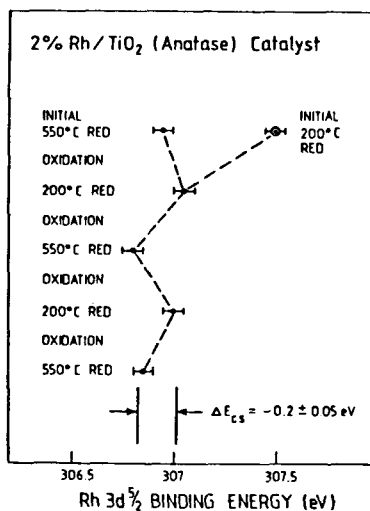


Figure 4. (From reference 33b)*

*Copyright ©, 1979, by Academic Press, Inc.

EVIDENCE INDICATES ELECTRON TRANSFER OCCURS FROM TITANIA TO THE METAL

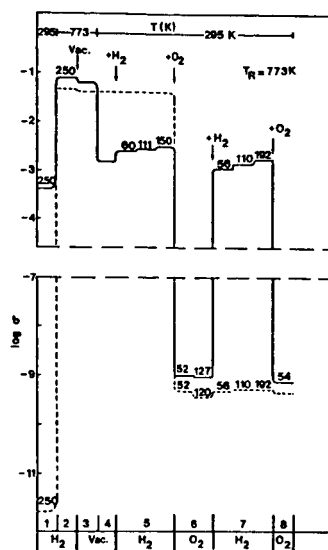


Binding energies of the Rh 3d $\frac{5}{2}$ peak on a 2% Rh/TiO₂ catalyst after several cycles of reduction and oxidation. Initially reduction at 200 and 550°C produces a large $\Delta E_{\text{TS}} = -0.6 \text{ eV}$ but this changes to -0.2 eV after an oxidation-reduction cycle.

Figure 5. (From reference 25)*

*Copyright ©, 1982, by Academic Press, Inc.

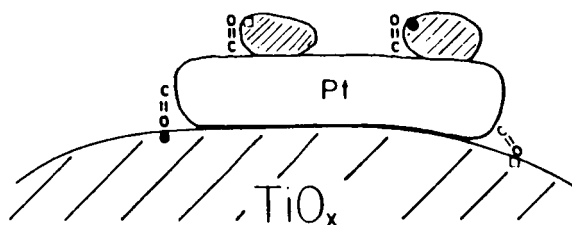
ORIGINAL PAGE IS
OF POOR QUALITY
CONDUCTIVITY CHANGES INDICATE
TRANSFER FROM TITANIA TO METAL



Logarithm of the electrical conductivity (in $\Omega^{-1} \text{ cm}^{-1}$) of TiO_2 (dotted line) and of the S-Pt sample (solid line) reduced at 773 K in H_2 as a function of the different phases described in the text; the numbers on the curves indicate the pressures (in Torr) of the corresponding gas.

Figure 6. (From reference 29)*

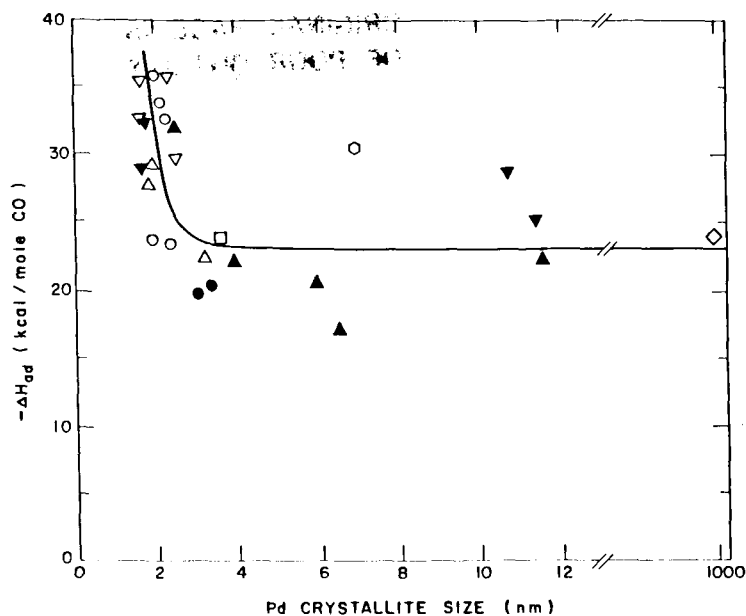
*Copyright ©, 1982, by Academic Press, Inc.



Proposed model for CO hydrogenation active sites in Pt-titania systems: (●) Ti^{3+} cation; (□) oxygen vacancy.

Figure 7. (From reference 69)*

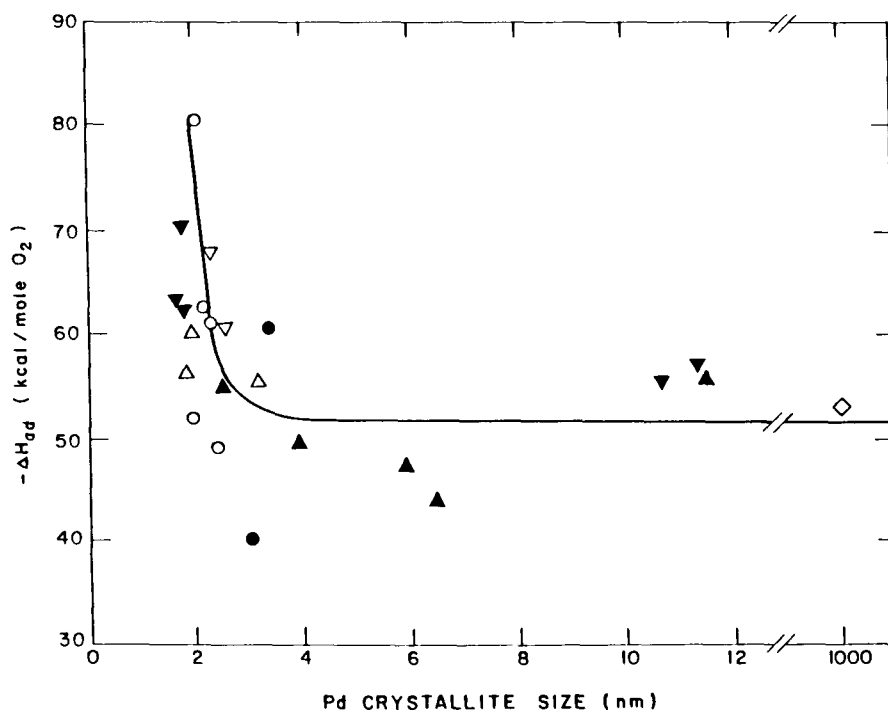
*Reprinted with permission, copyright ©, 1984, American Chemical Society.



Heats of adsorption of CO on supported and unsupported palladium:
 Pd/SiO₂ (▼, ▽), Pd/SiO₂-Al₂O₃ (▲, △), Pd/Al₂O₃ (●, ○), Pd/TiO₂
 (□, ◇), Pd powder (◇). Solid symbols: samples reduced at 673K;
 Open symbols: samples reduced at 573K or 448K.

Figure 8. (From reference 96)*

*Copyright ©, 1987, by Academic Press, Inc.



Integral heat of adsorption of oxygen on Pd at 300 K versus
 crystallite size : Pd/SiO₂ (▼, ▽); Pd/SiO₂-Al₂O₃ (▲, △); Pd/Al₂O₃
 (●, ○); Pd powder (◇); Solid symbols -- T_r = 673 K, open symbols --
 T_r = 448 K or 573 K.

Figure 9. (From reference 97)*

*Copyright ©, 1987, by Academic Press, Inc.