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Exhaust-Catalyst Development for Methanol-Fueled Vehicles

2. Synergism between Palladium and Silver in Methanol and Carbon Monoxide Oxidation over an Alumina-Supported Palladium–Silver Catalyst

R. W. McCabe and P. J. Mitchell

Physical Chemistry Department, General Motors Research Laboratories, Warren, Michigan 48090

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Methanol and carbon monoxide oxidation were examined over 0.01 Pd, 5% Ag, and 0.01% Pd/5% Ag catalysts—all supported on γ-alumina. The bimetallic catalyst showed greater CO and CH_3OH oxidation activity than either of the single-component catalysts; moreover, the Pd and Ag interacted synergistically in the bimetallic catalyst to produce greater CO and CH_3OH oxidation rates and lower yields of methanol partial oxidation products than expected from a mixture of the single-component catalysts. Temperature-programmed oxidation experiments and reactivity experiments involving changes in O_2 partial pressure both provided evidence that the Pd–Ag synergism results from Pd promoting the rate of O_2 adsorption and reaction with CO and CH_3OH on Ag. The data also indicate that virtually all of the Pd in the bimetallic catalyst is present in Pd–Ag crystallites. © 1987 Academic Press, Inc.

INTRODUCTION

This study is a continuation of research aimed at designing catalysts that efficiently oxidize exhaust pollutants from methanol-fueled vehicles. In our previous study (*1*), CO strongly inhibited CH_3OH oxidation over Pd and Pt but not over Ag. Consequently, a 1.92% Ag/γ-Al_2O_3 catalyst converted CH_3OH more efficiently at temperatures below 450 K in the presence of CO than did 0.054% Pt/γ-Al_2O_3 or 0.034% Pd/γ-Al_2O_3 catalysts. The Ag catalyst, however, was less active than the Pd and Pt catalysts at temperatures above 450 K, nor did it convert CO as effectively as the Pd and Pt catalysts. These results suggested that a catalyst containing both Ag and Pd (or Pt) would oxidize CO and CH_3OH with greater efficiency over the range of temperatures experienced in methanol-vehicle exhaust than catalysts containing either Pd, Pt, or Ag alone.

In addition to the multifunctional behavior predicted above (i.e., Ag for low-temperature CH_3OH oxidation; Pd or Pt for CO oxidation and high-temperature CH_3OH oxidation), we wished to prepare the bimetallic catalyst in such a way that synergistic interactions would occur between the metal components. Synergism is most likely to occur in catalysts where the metals are present as bimetallic crystallites. To this end, we (1) chose Pd rather than Pt (for greater miscibility with Ag (*2, 3*)), (2) utilized a low Pd-to-Ag ratio, and (3) employed preparative techniques that give uniform Pd and Ag distributions in the pellets (*4*).

The bimetallic approach is evaluated in this study based on results of CH_3OH and CO oxidation experiments carried out over a 0.01% Pd/5% Ag/γ-Al_2O_3 catalyst. Selectivity and activity data are compared to those obtained with 0.01% Pd/γ-Al_2O_3 and 5% Ag/γ-Al_2O_3 catalysts under identical reaction conditions.

EXPERIMENTAL

Reactor system. The reactor and experimental methods were identical to those employed previously (*1, 5*) and are only briefly reviewed here. The reactor was a 2.5-cm-o.d. quartz tube housed in a single-zone

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furnace. The feed gases passed downward through the reactor and sequentially contacted stacked layers of (1) quartz beads (for preheating the feed), (2) the catalyst pellets, and (3) quartz wool (for supporting the catalyst and quartz beads). Temperatures were measured with a Chromel–Alumel thermocouple positioned along the reactor centerline with its tip located in the catalyst bed a few millimeters below the top of the bed.

Catalyst activities and selectivities were compared using three feeds: (1) 0.2% CH_3OH, 1% O_2, balance He; (2) 0.2% CO, 1% O_2, balance He; and (3) 0.2% CH_3OH, 0.2% CO, 1% O_2, balance He. The space velocity in most runs was 52,000 h^{-1} (volume basis; standard conditions).

The products were analyzed principally with a Varian 6000 gas chromatograph equipped with both flame ionization and thermal conductivity detectors (*1*).

Temperature-programmed oxidation (TPO) system. Reduced forms of the 0.01% Pd, 5% Ag, and 0.01% Pd/5% Ag catalysts were characterized by temperature-programmed oxidation in a system separate from the reactor apparatus. The rate of activated O_2 uptake was measured by thermal conductivity detectors in a stream of 5% O_2/He which flowed at 15 cm^3 min^{-1}. The catalyst temperature was ramped at a rate of 7 K min^{-1}.

Catalysts. The catalysts were 3.5-mm diameter γ-alumina beads (Grace Chemical Co., 110 m^2 g^{-1} BET surface area, 0.5 g cm^{-3} apparent bulk density) impregnated with either Pd, Ag, or a combination of Pd and Ag. All impregnations were made from aqueous, minimum volume solutions of the metal salts—$Pd(NH_3)_4(NO_3)_2$ and $AgNO_3$. The impregnated catalysts were dried for 12 h at room temperature. The catalysts were subsequently heated in flowing air to 773 K where they were held for 4 h.

The bimetallic 0.01% Pd/5% Ag catalysts was prepared sequentially; the alumina support was first impregnated with $AgNO_3$, dried, and calcined as outlined above, and then the same procedure was repeated for the Pd ammine salt.

In a few cases involving Ag catalysts, a reducing pretreatment was employed rather than the calcination described above. The dried catalyst was reduced by washing in aqueous formaldehyde solution and subsequently heated in flowing 5% H_2/N_2 at 573 K for 4 h.

The 0.01% Pd catalyst had a dispersion of 42% as measured by static chemisorption at 308 K, assuming a stoichiometry of 1 CO molecule per exposed Pd atom. The dispersion of the air-calcined 5% Ag catalyst was 27% as measured by O_2 chemisorption using techniques similar to those of Vannice and co-workers (*6, 7*). Attempts to measure Pd-atom dispersion in the bimetallic catalyst were unsuccessful. The small amount of irreversibly adsorbed CO associated with the Pd could not be distinguished from the large amount of reversibly adsorbed CO associated with the Ag.

RESULTS AND DISCUSSION

I. Pd–Ag Synergism in CH_3OH and CO Oxidation

The principal observations of importance to methanol vehicle exhaust are shown in Figs. 1 and 2, where methanol conversion

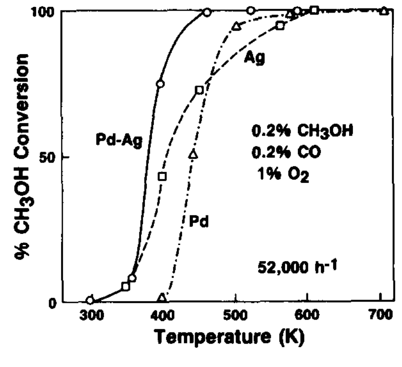

FIG. 1. Percentage conversion of CH_3OH as a function of temperature for 0.01% Pd/γ-Al_2O_3, 5% Ag/γ-Al_2O_3, and 0.01% Pd/5% Ag/γ-Al_2O_3 catalysts. The feed contained 0.2% CH_3OH, 0.2% CO, and 1% O_2 in He carrier. The space velocity was 52,000 h^{-1} in all cases.

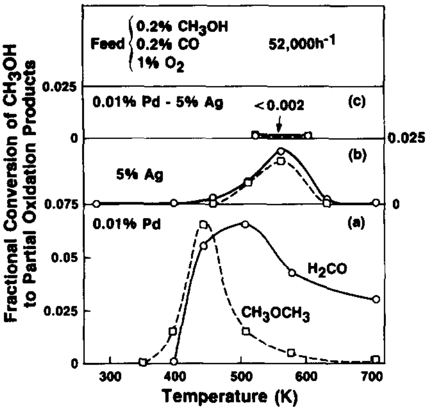

FIG. 2. Yields of CH_3OH partial oxidation products as a function of temperature over (a) 0.01% Pd/γ-Al_2O_3, (b) 5% Ag/γ-Al_2O_3, (c) 0.01% Pd/5% Ag/γ-Al_2O_3. The squares represent dimethyl ether and the circles formaldehyde. The feed contained 0.2% CH_3OH, 0.2% CO, and 1% O_2 in He carrier at a space velocity of 52,000 h^{-1}. Yields are expressed as the mole fraction of the feed methanol converted to each species.

and product selectivity are compared for the alumina-supported 0.01% Pd, 5% Ag, and 0.01% Pd/5% Ag catalysts as a function of temperature. The comparisons are made for a feed containing CO in addition to CH_3OH and O_2. Figure 1 shows that the Pd/Ag catalyst is more active than either the Ag or Pd catalyst alone, achieving 50% conversion of CH_3OH at 380 K versus 405 K for the Ag catalyst and 440 K for the Pd catalyst. Moreover, the Pd/Ag catalyst displays synergism between Pd and Ag as evidenced by the enhanced conversion of the Pd/Ag catalyst relative to the Ag catalyst at temperatures below 400 K where the Pd catalyst is inactive. Synergism is also demonstrated in Fig. 2 where the Pd/Ag catalyst produces much lower yields of partial oxidation products (dimethyl ether and formaldehyde) than either the Ag or Pd catalyst.

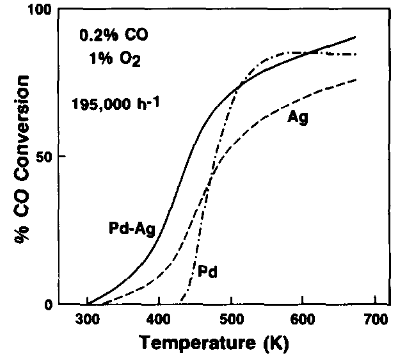

FIG. 3. Percentage conversion of CO as a function of temperature for 0.01% Pd/γ-Al_2O_3, 5% Ag/γ-Al_2O_3, and 0.01% Pd/5% Ag/γ-Al_2O_3 catalysts. The feed contained 0.2% CO and 1% O_2 in He carrier. The space velocity was 195,000 h^{-1} in all cases.

The Pd/Ag catalyst also shows greater CO oxidation activity than either the Pd or Ag catalyst, as shown in Fig. 3 for data obtained at a space velocity of 195,000 h^{-1}. The shape of the CO conversion profile obtained with the Pd/Ag catalyst is similar to that obtained with the Ag catalyst but is displaced to higher conversion levels over the entire temperature range examined. This suggests that oxidation of carbon monoxide by the bimetallic catalyst occurs principally on Ag sites but is promoted in some manner by Pd.

II. Mechanism of Pd Promotion

Figure 4 shows results of CH_3OH oxidation experiments using the 0.01% Pd, 5% Ag, and 0.1% Pd/5% Ag catalysts in the absence of CO. Compared to the experiments

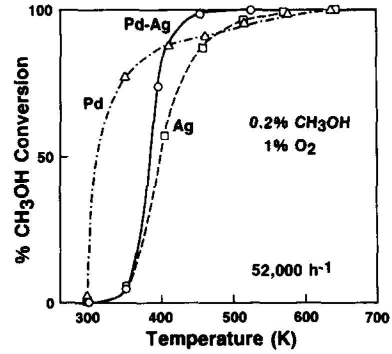

FIG. 4. Percentage conversion of CH_3OH as a function of temperature for 0.01% Pd/γ-Al_2O_3, 5% Ag/γ-Al_2O_3, and 0.01% Pd/5% Ag/γ-Al_2O_3 catalysts. The feed contained 0.2% CH_3OH and 1% O_2 in He carrier. The space velocity was 52,000 h^{-1} in all cases.

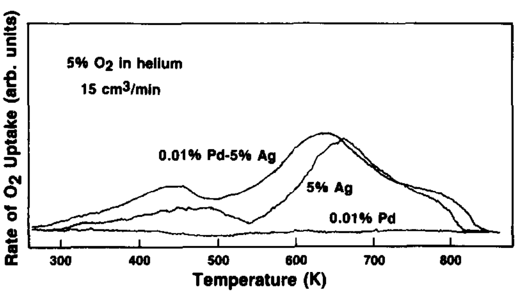

FIG. 5. Temperature-programmed oxidation data for reduced 0.01% Pd/γ-Al_2O_3, 5% Ag/γ-Al_2O_3, and 0.01% Pd/5% Ag/γ-Al_2O_3 catalysts. The rate of O_2 uptake by each catalyst is plotted as a function of temperature. The feed contained 5% O_2 in He at a flow rate of 15 cm^3 min^{-1}. 0.1 g of catalyst was used in each case.

carried out in the presence of CO (Fig. 1), the biggest difference is for the Pd catalyst, which shows a tremendous increase in low-temperature activity when CO is removed from the feed. The Ag catalyst, in contrast, is only slightly more active in the absence of CO than in the presence of CO. Both of the above observations are consistent with results of our previous study (*1*). In that work, strong inhibition of CH_3OH oxidation was observed for Pd and was attributed to the blocking of CH_3OH chemisorption sites by strongly adsorbed CO. For Ag, which adsorbs CO weakly, a similar site-blocking was not observed.

The most interesting comparison between Figs. 4 and 1 is for the bimetallic catalyst which shows identical methanol conversion profiles in the presence and absence of CO. This indicates that the enhanced activity of the bimetallic catalyst compared to the Ag catalyst does not result from differences in the way CO interacts with the bimetallic catalyst versus the Ag catalyst. Moreover, since the bimetallic catalyst enhanced both CO and CH_3OH oxidation, the mechanism of Pd promotion cannot be ascribed to an effect involving CO alone or CH_3OH alone. The above arguments suggest that the rate enhancement observed with the Pd/Ag catalyst does not result from a reduction of CO desorption energy for Pd when alloyed with Ag (*8*): instead, they suggest that, for these bimolecular oxidation reactions, Pd promotes a reaction step involving O_2 rather than CO or CH_3OH.

We next examine the role of O_2 by analyzing (1) TPO experiments and (2) CH_3OH oxidation experiments over a 2% Ag catalyst at two O_2 concentrations. Figure 5 shows rates of activated O_2 uptake for a feed containing 5% O_2/He which flowed at 15 cm^3 min^{-1} over 0.1-g samples of each of the three catalysts. The sensitivity of the instrument was too low to detect any O_2 uptake by the 0.01% Pd sample. The rates of O_2 uptake on both the Ag and Pd/Ag catalysts peaked at two temperatures. The bimetallic catalyst showed lower peak temperatures (by about 25 K) and a greater rate of O_2 uptake than the Ag catalyst at temperatures below 650 K.

The natures of the two peaks observed in Fig. 5 are not known. Thermodynamic calculations rule out the formation of bulk Ag_2O as an explanation for either peak, as bulk Ag_2O would not be stable at temperatures above ~390 K in the 5% O_2/He feed. The peak appearing between 450 and 500 K in the Pd/Ag and Ag catalysts may be associated with an activated dissociative chemisorption of O_2 since the peak temperature correlates closely with temperatures routinely employed in dissociative O_2 chemisorption measurements on supported Ag catalysts (*6, 7*). Also, Czanderna reported that the amount of O_2 adsorbed on Ag powder goes through a broad maximum between 400 and 475 K (*9*).

Since O_2 uptake was not observed for Pd alone in Fig. 5, *the enhanced rate of uptake observed for the Pd/Ag catalyst compared to the Ag catalyst indicates that Pd promotes the rate of* O_2 *uptake on Ag*. This observation is consistent with the relatively high sticking probabilities reported for dissociative O_2 chemisorption on Pd surfaces ($s_0 \sim 10^0$ (*10*)) compared to the extremely low values reported for Ag surfaces ($s_0 = 10^{-6}$–10^{-4} (*11, 12*)).

Additional experiments were carried out with a 2% Ag/γ-Al_2O_3 catalyst to examine the effects of O_2 partial pressure on CH_3OH oxidation rate and selectivity. Data for feeds containing 0.25% and 1% O_2 are shown in Fig. 6. At temperatures below 400 K, conversions were nearly identical, but the conversions were greater for the 1% O_2 feed at higher temperatures. Thus below 400 K, the CH_3OH oxidation rate is low and the O_2 adsorption rate is not a limiting factor. Above 400 K, however, the CH_3OH oxidation rate increases to the point where the rate of O_2 supply affects the overall conversion. The differences between the conversions observed for the 0.25% O_2 feed compared to the 1% O_2 feed increase up to ~540 K and then decrease at higher temperatures. The CH_3OH conversion of ~85%, observed for the 0.25% O_2 feed at 540 K, is close to the theoretical conversion of 83% for complete consumption of the feed O_2. Thus the continued increase in conversion observed for CH_3OH in the 0.25% feed above 540 K results from CH_3OH decomposition, as evidenced by both a leveling off of the CO_2 yield (not shown) and by a concomitant increase in CO yield (shown in Fig. 6).

The effect of increasing the O_2 concentration from 0.25 to 1% over the 2% Ag catalyst is similar to the effect of adding 0.01% Pd to the 5% Ag catalyst (compare Figs. 6 and 4). In both cases, the conversion profiles are identical at low temperatures and diverge at higher temperatures, with the higher conversions resulting from a higher O_2 concentration in one case (Fig. 6) and the presence of Pd in the other case (Fig. 4). Moreover, just as adding 0.01% Pd to the 5% Ag catalyst decreased the yield of partial oxidation products (cf. Fig. 2), a smaller yield of partial oxidation products was observed when the feed O_2 concentration was increased from 0.25 to 1% over the 2% Ag catalyst.

In summary, the combined O_2 partial pressure and TPO experiments indicate that (1) at most temperatures, the rate of O_2 supply influences both the overall CH_3OH oxidation rate and the selectivity over the Ag and Pd/Ag catalysts, (2) Pd promotes the rate of O_2 uptake on Ag in the bimetallic catalyst, and (3) the rate of O_2 uptake on Ag and the selectivity for complete oxidation can both be increased either by increasing the feed O_2 concentration or by adding Pd to the Ag catalyst.

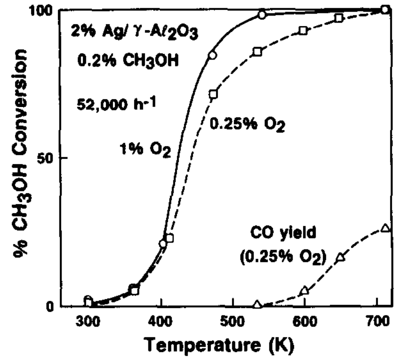

FIG. 6. Percentage CH_3OH conversion as a function of temperature for CH_3OH oxidation over a 2% Ag/γ-Al_2O_3 catalyst at feed O_2 concentrations of 0.25% (dashed curve) and 1% (solid curve). The feed contained 0.2% CH_3OH in He carrier at a space velocity of 52,000 h^{-1} in both experiments. For the 0.25% O_2 feed, the CO_2 yield peaked near 85% CH_3OH conversion and higher CH_3OH conversions resulted from decomposition of CH_3OH as indicated by the CO yields observed above 540 K.

III. *Distribution of Pd and Ag in the Bimetallic Catalyst*

The mechanism of Pd promotion, involving enhancement of dissociative O_2 adsorption, suggests the presence of bimetallic crystallites; in bimetallic crystallites, oxygen atoms, formed by O_2 adsorption and dissociation at Pd surface atoms, can subsequently diffuse onto Ag surface atoms and react with CO or CH_3OH. We next examine the data for evidence that provides insight into the nature of the distribution of Pd and Ag in the bimetallic catalyst.

Figure 7 shows the possible distributions that Pd and Ag can take in the bimetallic catalyst: (a) complete separation of Pd and

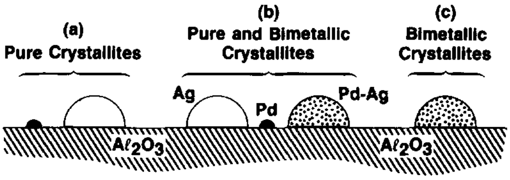

FIG. 7. Possible distributions of Pd and Ag in the 0.01% Pd/5% Ag/γ-Al_2O_3 catalyst: (a) pure crystallites of Pd and Ag, (b) pure and bimetallic crystallites of Pd and Ag, and (c) bimetallic crystallites only.

Ag into pure crystallites, (b) partial separation of Pd and Ag resulting in a mixture of pure and bimetallic crystallites, and (c) no separation of Pd and Ag (i.e., bimetallic crystallites only). We do not address the question of how Pd and Ag are distributed between the surface and the bulk in the case of bimetallic crystallites.

Distribution (a) can be dismissed by referring to the data of Fig. 4. The Pd catalyst is much more active than the Ag catalyst for CH_3OH oxidation in the absence of CO. If the Pd/Ag catalyst contained segregated Pd and Ag crystallites, the Pd crystallites would dominate the activity, and the conversion profile for the Pd/Ag catalyst would be identical to that for the Pd catalyst. However, the conversion profile for the Pd/Ag catalyst in Fig. 4 more closely resembles that of the Ag catalyst.

Distributions (b) and (c) can be distinguished on the basis of CH_3OH oxidation selectivity. As shown in Fig. 8, CH_3OH oxidation over the Pd catalyst (in the absence of CO) produced significant yields of CH_3OCHO and H_2CO. In contrast, CH_3OH oxidation over the Pd/Ag catalyst under identical conditions produced no detectable partial oxidation products. The absence of partial oxidation products characteristic of Pd in the case of the bimetallic catalyst suggests that all of the Pd in the bimetallic catalyst is associated with Ag (i.e., distribution (c)). However, care must be taken in proposing distribution (c) to ensure that the absence of partial oxidation products does not result instead from the following concerted mechanism: (1) Pd converts CH_3OH to partial oxidation products and (2) Ag efficiently converts the partial oxidation products to CO_2 and H_2O. Such a scenario could be consistent with distributions (a) and (b).

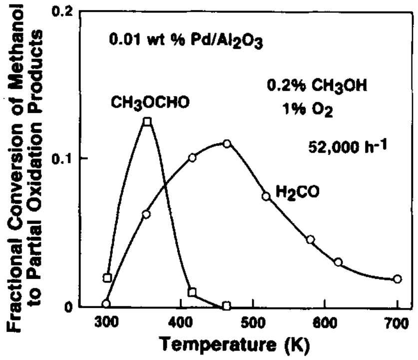

FIG. 8. Yields of CH_3OH partial oxidation products as a function of temperature over the 0.01% Pd/γ-Al_2O_3 catalyst. The feed contained 0.2% CH_3OH and 1% O_2 in He at a space velocity of 52,000 h^{-1}.

To explore the possibility of a concerted mechanism, experiments were carried out comparing CH_3OH oxidation over the 0.1% Pd/5% Ag catalyst with CH_3OH oxidation over a physical mixture of 0.01% Pd catalyst and 5% Ag catalyst. The amounts of Pd and Ag were identical in the two cases. Selectivity data for H_2CO and CH_3OCHO are

TABLE 1

Comparison of CH_3OH Oxidation Selectivities: Bimetallic Catalysts vs Physical Mixture

Description	Reactor charge	Max. H_2CO yield[a] (ppm)	Max. CH_3OCHO yield (ppm)
Bimetallic catalyst	0.01% Pd/5% Ag (7.5 cc) + blank Al_2O_3 (7.5 cc)	Nd[b]	ND
Physical mixture	0.01% Pd (7.5 cc) + 5% Ag (7.5 cc)	42	95
Pd only	0.01% Pd (15 cc)	220	125
Pd only	0.01% Pd (4 cc)	415	25

Note. The feed, in all cases, contained 2000 ppm CH_3OH and 1% O_2 in He at a flow rate of 13 liters min^{-1}. Small amounts of CH_3OCH_3 were also detected in some cases, but are not included since CH_3OCH_3 is produced by reaction of CH_3OH with the Al_2O_3 support (*1*).

[a] Maximum H_2CO concentration observed while oxidizing the feed containing 2000 ppm CH_3OH at temperatures between 300 and 700 K.

[b] ND = not detected (i.e., H_2CO concentration was less than 5 ppm and CH_3OCHO concentration was less than 10 ppm).

summarized in Table 1, which also contains data for the 0.01% Pd catalyst at two reactor loadings. The maximum H_2CO yield obtained with the physical mixture was much lower than those obtained with the Pd catalyst. This confirms that the Pd and Ag catalysts work in concert; Ag oxidizes much of the H_2CO produced by the Pd catalyst.

Despite evidence for a concerted mechanism between the Pd and Ag catalysts, Table 1 shows that H_2CO and CH_3OCHO were detected in all cases where pure Pd catalysts were contained in the reactor, but not in the case of the bimetallic catalyst. The absence of partial oxidation products over the Pd/Ag catalyst provides evidence that all of the Pd is present together with Ag in bimetallic crystallites. Thus we conclude that distribution (c) in Fig. 7 most accurately characterizes the 0.1% Pd/5% Ag catalyst.

ACKNOWLEDGMENT

Dr. Michael J. D'Aniello, Jr., carried out the chemisorption analyses on the Pd and Ag catalysts.

REFERENCES

1. McCabe, R. W., and Mitchell, P. J., *Appl. Catal.* **27,** 83 (1986).
2. Hanson, M., "Constitution of Binary Alloys," pp. 41–45. McGraw–Hill, New York, 1958.
3. Shunk, F. A., "Constitution of Binary Alloys, Second Supplement," pp. 7, 8. McGraw–Hill, New York, 1969.
4. D'Aniello, M. J., Jr., *J. Catal.* **69,** 9 (1981).
5. McCabe, R. W., and Mitchell, P. J., *Ind. Eng. Chem. Prod. Res. Dev.* **22,** 212 (1983); **23,** 196 (1984).
6. Seyedmonir, S. R., Strohmayer, D. E., Geoffroy, G. L., Vannice, M. A., Young, H. W., and Linowski, J. W., *J. Catal.* **87,** 424 (1984).
7. Seyedmonir, S. R., Strohmayer, D. E., Guskey, G. J., Geoffroy, G. L., and Vannice, M. A., *J. Catal.* **93,** 288 (1985).
8. Noordermeer, A., Kok, G. A., and Nieuwenhuys, B. E., *Surf. Sci.* **165,** 375 (1986).
9. Czanderna, A. W., *J. Phys. Chem.* **68,** 2765 (1964).
10. Conrad, H., Ertl, G., Kuppers, J., and Latta, E. E., *Surf. Sci.* **65,** 245 (1977).
11. Campbell, C. T., *Surf. Sci.* **157,** 43 (1985) and references therein.
12. Albers, H., Vander Wal, N. J., Gijzeman, O. L. J., and Bootsma, G. A., *Surf. Sci.* **77,** 1 (1978).