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Role of Surface Composition in CO Adsorption on Pd–Ag Catalysts[1]

One of the important problems in the study of metal-alloy catalysts is the surface composition of the multicomponent metal system. With the advent of Auger electron spectroscopy (AES) the elemental composition of the surface layer (to a depth of a few atomic distances) can be sampled and quantitatively characterized. This technique has been applied to a number of mixed metals (*1*), including the Pd–Ag system (*2*), which forms disordered solid solutions over the entire composition range (*3*). As described in detail in Ref. (*2*), a series of alumina-supported Pd–Ag catalysts of different metal composition were prepared (2% weight loading of total metal). They were reduced in hydrogen at 625 K for 4 hr and subsequently annealed in argon at 975 K for 4 hr yielding crystallites with an average diameter of about 100 Å. For surface analysis the Auger electron signal intensities of the $M_5N_{4,5}N_{4,5}$ transitions of Pd (331 eV) and of Ag (at 350 eV) were employed. It is estimated that the escape depth of these Auger electrons is less than three atomic layers (*4*). Thus the intensities of the Auger lines of these mixed-metal catalysts are interpretable in terms of the concentration of the respective metal species near the surface of the crystallites. Thermodynamically the large difference in surface free energies of the two metal components, Pd and Ag, favors surface enrichment with respect to Ag, in accordance with the monolayer or multilayer equilibrium models of regular solutions (*5, 6*). The degree of surface enrichment with silver, as determined in our experimental study (*2*), is shown in Fig. 1, in which we have plotted the excess silver to be found on the surface relative to that of the bulk phase. Qualitatively the trend towards silver enrichment was deduced from photoelectron emission studies of thin films of Pd–Ag alloys (*7*).

In view of the silver enrichment on the surface of the Pd–Ag crystallites we have reexamined the CO-adsorption studies carried out by Soma-Noto and Sachtler (*8*) who considered the surface composition to be identical to that of the bulk. Although our elemental surface analysis of the Pd–Ag system was done with an alumina-supported catalyst (*2*) and the CO-adsorption studies involved a silica-supported catalyst (*8*), there is no indication of any influence of the type of support on the composition of the alloy crystallites. The infrared spectra of the CO-admolecules on the SiO_2-supported alloy catalysts are interpreted in terms of the Eischens–Pliskin structures, a bridged type with stretching frequencies at less than 1940 cm^{-1} and a linear type with stretching frequencies at greater than 2045 cm^{-1}. Of special interest is the variation in the fraction of bridge-bonded CO-admolecules with mixed-metal composition of the catalyst. These results are shown in Fig. 2 in which the original data (*8*) have been replotted in terms of the surface composition as deduced from the observed AES of the Pd–Ag system. Such a correlation with surface composition exhibits a linear decrease in the fraction of bridge-bonded CO as Ag atoms are admixed to the Pd surface atoms. From the experimental ratio of bridge- to

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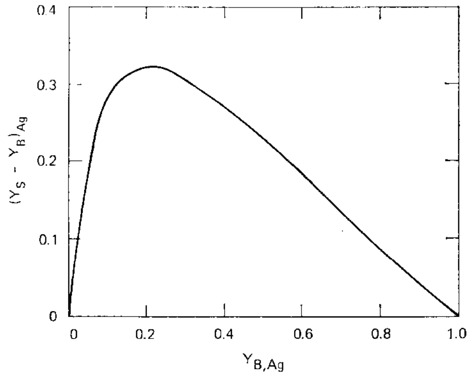

FIG. 1. Deviation of surface from bulk composition for Pd–Ag alloy (Y_B and Y_s represent the metal atom fractions in the bulk and at the surface).

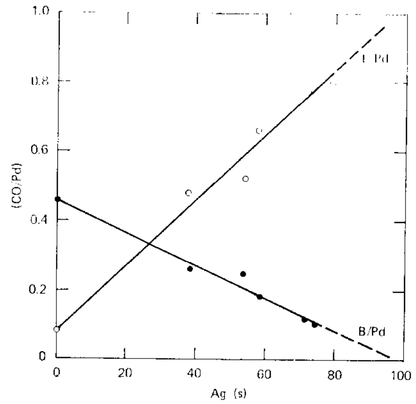

FIG. 3. Fraction of bridge (B/Pd)- and linear (L/Pd)-bonded CO as a function of surface composition of SiO_2-supported Pd–Ag alloy.

linear-bonded CO we can compute the CO/Pd ratio for each of these two configurations (Fig. 3), on the assumption that the absorption cross section for each adspecies is the same. These results indicate that in the formation of surface bonds with carbon monoxide admolecules an electronic effect is not demonstrable.

Rather the process of bond formation for bridge CO-admolecules is governed by the geometric requirement of two or more neighboring Pd-surface atoms. This problem in the statistics of "ensembles" of surface alloys has been explored by Dowden (*9*). The probability of finding two or more nearest neighbors of the same type in an ensemble containing five atoms, as applies for example to the (100) face of a fcc structure, can be calculated as a function of the composition of the disordered binary alloy. In Table 1 we compare this probability ($P'_{5,2}$) with the fractional bridge-bonded surface coverage of CO for different Pd/Ag surface compositions. The ensemble analysis predicts to a high degree of approximation the experimentally observed results when account is taken of the difference between surface and bulk composition of the alloy. Thus

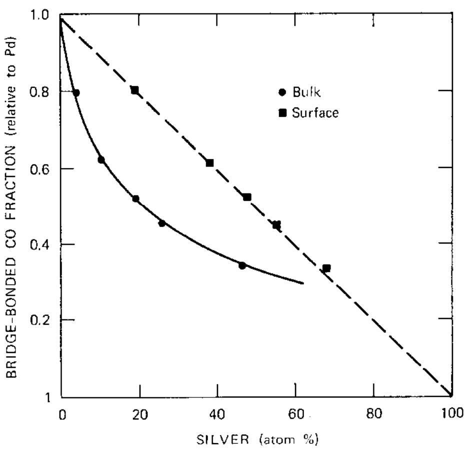

FIG. 2. Variation in relative fraction of bridge-bonded CO with Pd–Ag alloy composition [SiO_2-supported catalyst (*8*)].

TABLE 1

Ensemble Effect in CO Adsorption on SiO_2 Supported Pd–Ag Catalysts

Surface composition (atom %)		CO(B)/Pd[a]	$P'_{5,2}$
Pd	Ag		
100	0	1.00	1.00
62	38	0.56	0.62
42	58	0.37	0.39
29	71	0.24	0.23

[a] Ratio of bridge-bonded CO admolecules per surface Pd atom for the alloy relative to that for Pd as calculated from the results reported in Ref. (*8*).

in the case of CO adsorption, the Ag-atom on the surface merely dilutes the number of near-neighbor Pd atoms in the ensemble which are required for bridge-bonded CO chemisorption. It is concluded that in this mixed metal-adsorbate system the electronic ligand effect associated with *d*-band filling is absent as suggested in Ref. (*8*). Similar considerations apply to a more recent study of CO adsorption on supported Pd–Ag alloys (*10*). However, deviation from the equilibrium surface composition caused by prolonged exposure to reactive gases represents a problem worthy of further study (*2*, *7*).

REFERENCES

1. Chester, M. A., and Somorjai, G. A., *Annu. Rev. Mater. Sci.* **5**, 99 (1975).

2. Wood, B. J., and Wise, H., *Surface Sci.* **52**, 151 (1975).

3. Darby, J. B., Jr., *Acta Met.* **14**, 265 (1966).

4. Palmberg, P. W., *Anal. Chem.* **45**, 549A (1973).

5. Van Santen, R. A., and Boersma, M. A., *J. Catal.* **34**, 13 (1974).

6. Williams, F. R., and Mason, D., *Surface Sci.* **45**, 377 (1974).

7. Bouwman, R., Lippits, G. J. M., and Sachtler, W. M. H., *J. Catal.* **25**, 350 (1972).

8. Soma-Noto, T., and Sachtler, W. M. H., *J. Cat.* **32**, 315 (1974).

9. Dowden, D. A., *Proc. Int. Congr. Catal., 5th, 1972* **1**, 621 (1973).

10. Cormack, D., Pritchard, J., and Moss, R. L., *J. Catal.* **37**, 548 (1975).

Henry Wise

Solid State Catalysis Laboratory
Stanford Research Institute
Menlo Park, California 94025

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