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CO Chemisorption on Silica-Supported Palladium–Silver Alloys

It was shown recently that silver–palladium alloys containing from 75 to 95 atom% Ag, and supported on silica, were homogenized by heat treatment at 400°C (*1*). Evidence from X-ray diffraction was substantiated by comparing the composition-related variation of selectivity in ethylene oxidation for these supported alloys with the selectivity pattern observed previously (*2*) using evaporated alloy films. The choice of selectivity rather than specific activity avoided uncertainty associated with (alloy) surface area measurements in supported alloys by the chemisorption method, viz, the effect of alloy composition on the surface metal atom/adsorbate molecule ratio. However, as in the case of supported *pure metal* catalysts, it will often be essential to measure the surface area of a supported *alloy*. This note reports such an attempt for palladium-rich supported Pd–Ag alloys on which carbon monoxide chemisorption is known to occur.

Catalysts were prepared by impregnating silica (Davison, grade 70) with solutions containing silver nitrate and tetramminepalladous nitrate. The appropriate weight of each salt was dissolved in 50 ml distilled water and 20 g silica were added to produce a slurry which was mixed until a uniform consistency was obtained before drying at 60°C overnight. Catalysts had a metal loading of 4% by weight and alloy compositions were in the range 50–100 atom% Pd. After the standard firing treatment (400°C in air for 3 hr), samples for CO chemisorption (about 1 g) were purged with nitrogen and reduced in a flow of pure hydrogen at 400°C for 2 hr, then outgassed overnight at 350°C. The equipment for CO chemisorption measurements has been described previously (*3*). After CO chemisorption had been measured, the samples were examined by X-ray diffraction, using a counter-diffractometer, with respect to bulk homogeneity (lattice constant, peak symmetry) crystallite size (from peak breadth) and detectable metal (intensity of diffraction peak relative to an internal MgO standard). The procedure for estimating detectable metal has also been described previously (*3*).

The homogeneity of the alloys prepared and the extent to which they have been dispersed into small crystallites are first established. Table 1 compares the lattice constant for bulk alloys (*4*) with observed values for our supported alloys; only (111) diffraction peaks could be recorded but, based on the comparison of expected and observed values for pure Pd, the resulting error is small. The mean deviation for this series of supported alloys (subjected to the standard firing, reduction and outgassing treatment) is the same as that observed previously (*1*) for silver-rich alloys (supported on silica) which had been directly reduced at 400°C but for longer periods [treatment C, Ref. (*1*)] and which had been shown to be well alloyed.

Two quantities in Table 1 measure the extent to which the alloy has been dispersed, viz, the crystallite size, D, and the relative intensity, α, as defined below. The area of the diffraction peak rising above the general baseline is diminished, *inter alia*, by the presence of highly dispersed alloy which is not included in the average crystallite size measured. Theoretical val-

TABLE 1
X-RAY DATA FOR SUPPORTED PD-AG ALLOYS

	Lattice constant (Å)		Metal dispersion		
Composition (atom% Pd)	Expected for a bulk alloy (*4*)	Observed	Crystallite size D (Å)	Relative intensity α	Classification[a]
100	3.891	3.90_4	110	1.28	(i)
100[b]	3.891	3.90_4	80	1.59	(ii)
90	3.907	3.92_2	80	1.28	(i)
80	3.924	3.92_7	100	1.25	(i)
80[c]	3.924	3.91_4	110	1.48	(ii)
70	3.942	3.94_2	120	1.37	(i)
60	3.960	3.96_6	100	1.55	(ii)
50	3.979	3.97_0	90	1.28	(i)
50[c]	3.979	3.97_1	100	1.36	(i)

[a] See text for explanation.

[b] Fired at 800°C.

[c] Outgassed for 65 hr at 350°C.

ues of the relative intensity, α, where

$$\alpha = \text{area Pd(111) diffraction peak/area MgO(200) diffraction peak},$$

were calculated, using MgO as an internal standard. For a reference system containing 4% Pd or 4% Ag and 10% MgO by weight, the respective α-values calculated are 1.82 for supported Pd catalysts and 1.92 for supported Ag catalysts. Such α-values might be expected in well-sintered catalysts but, in practice, are not attained due to X-ray absorption effects when the crystallites become aggregated (*3*). When (pure) Pd supported on silica was progressively sintered at temperatures between 400 and 1000°C, the α-values accordingly passed through a maximum, $\alpha = 1.6$, at 800-900°C.

Accordingly, two groups of catalysts can be distinguished in Table 1 on the basis of crystallite dispersion: (i) catalysts with α significantly less than 1.6 indicating that all the alloy present has not been included in the average crystallite size measured and with $D = 100 \pm 20$ Å and (ii) catalysts with $\alpha \sim 1.5-1.6$, considered sufficiently well sintered for the crystallite size to be used to calculate the alloy area.

Chemisorption of CO on the first group of catalysts at 25°C yielded isotherms, as illustrated by Fig. 1, where the adsorptive capacity decreased with decreasing Pd content but without introducing any difficulty in determining monolayer adsorption. Figure 2 (upper part) summarizes the variation of CO chemisorption (ml CO/g catalyst) with the alloy composition; catalysts of the first group ($\alpha \sim 1.25-1.40$; $D = 100 \pm 20$ Å) are identified by filled circles. Carbon monoxide did not adsorb at 25°C on a corresponding pure Ag-silica catalyst. Clearly, the specific adsorptive capacity does not fall linearly between silica-supported 100 atom% Pd and 100 atom% Ag catalysts, *although the crystallite dispersion is believed to be similar throughout this first group of alloy catalysts.* Two aspects of this result require comment, viz, its possible interpretation in terms of surface enrichment by silver and its application in surface area measurement.

Surface enrichment must always be con-

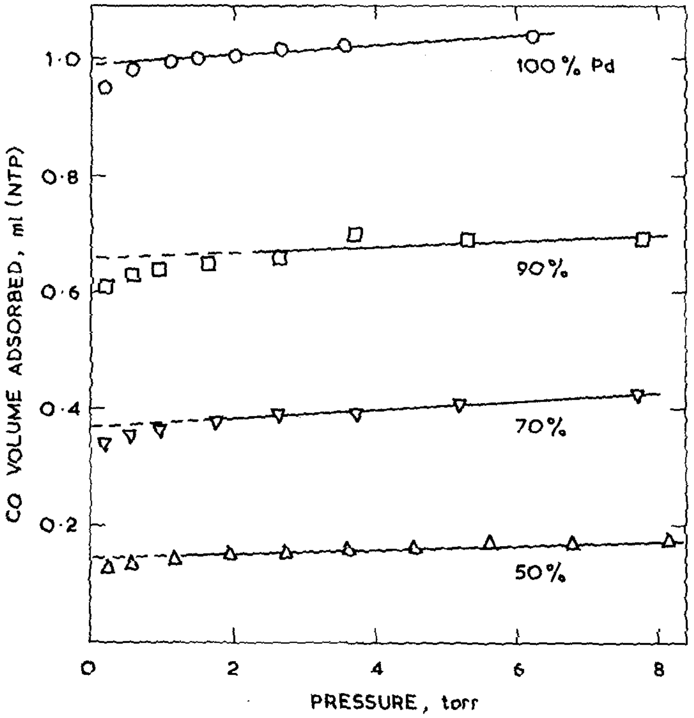

Fig. 1. CO adsorption at 25°C on silica-supported Pd or Pd–Ag catalysts, 4 wt% metal or alloy loading, with compositions (atom%) indicated; sample weights were: 100% Pd, 0.796 g; 90% Pd, 0.839 g; 70% Pd, 0.969 g; 50% Pd, 0.966 g.

sidered when working with alloy catalysts, arising as a consequence of either Gibbs enrichment by the component of lower surface energy or induced by chemisorption. Therefore, it is of interest to compare the present results for supported Pd–Ag alloys fired and reduced at 400°C, with the data of Christmann and Ertl (*5*) on Pd–Ag films, which were shown by Auger spectroscopy to have approximately equal surface and bulk compositions. The lower part of Fig. 2 shows the variation of work function after CO adsorption on the (111) and (100) planes of Pd–Ag alloy films, prepared by simultaneous vacuum evaporation and annealed at temperatures up to 400°C (*5*). The work function changes were independent of the nature of the crystal plane and also agreed well with results obtained using polycrystalline Pd–Ag films annealed at 300°C (*6*). The fall in $\Delta\Phi$ with addition of silver appears to indicate decreasing CO coverage, which was not independently measured, although the dipole moment of the adsorbate may become smaller. The similarity of the two plots in Fig. 2 can therefore only be noted, but one should remember that the upper plot was obtained with Pd–Ag alloys where the absence of surface enrichment by silver had been demonstrated.

The measurement of the area of the alloy component of supported Pd–Ag catalysts is considered next. The curve drawn through the filled circles in Fig. 2 (upper part) provides a "calibration" for use when comparing the (alloy) surface area using CO chemisorption, *on the basis that these points relate to catalysts with similar dispersions.* The relative dispersion of the alloy component can be found for "unknown" samples of Pd–Ag catalysts even though they have different alloy compositions. The further use of this calibration

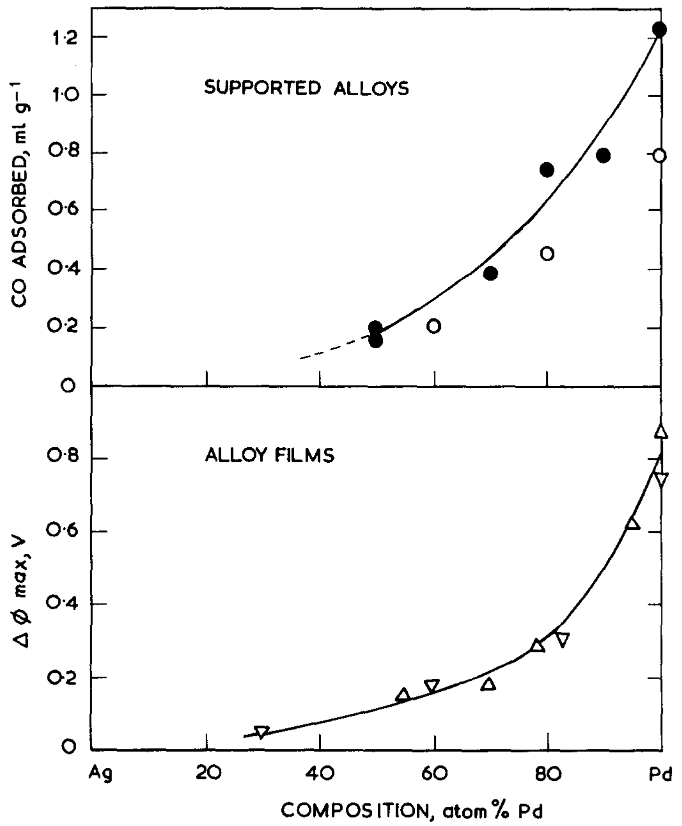

FIG. 2. (Upper part) CO adsorption on supported Pd–Ag alloys as a function of composition (present work). See text for explanation of symbols. (Lower part) Maximum work function change due to CO adsorption on (111) (△), and (100) (▽), planes of Pd–Ag alloy films; after Ref. (*5*).

curve is shown by the following example, where the metal or alloy surface area for the three catalysts identified by open circles in Fig. 2 (upper part) was examined. On the basis that (surface atom)/CO ratio for supported palladium is unity, and that the mean area of each palladium atom exposed is 7.9 Å^2 (*3*), the metal area for the more sintered (100%) palladium catalyst (Table 1) was 1.68 m^2/g catalyst. From CO chemisorption, the alloy areas in the more sintered 80% Pd and 60% Pd catalysts would be 0.96 and 0.43 m^2/g catalyst, without correction for the effect of composition. Correcting for the effect of composition, using the curve of Fig. 2 (upper part), these alloy areas become 1.83 and 1.81 m^2/g catalyst, respectively. Thus, the three catalysts have similar areas, i.e., 1.7–1.8 m^2/g catalyst.

The areas presented by the alloy crystallites were also calculated from the X-ray data in Table 1, assuming that the crystallites were cubes exposing five faces (*7*), using the appropriate density for the alloy concerned and assuming that the α-values were sufficiently high to ensure that the crystallite sizes measured represented a mean for all the crystallites present. The alloy areas calculated were 2.1, 1.6 and 1.8 m^2/g for these sintered catalysts with compositions at 100, 80 and 60% Pd, respectively. Therefore, similar areas are again indicated for the three catalysts, i.e., 1.6–2.1 m^2/g catalyst, which also agree reasonably well with corrected areas derived from CO chemisorption.

Thus, the areas of these supported Pd–Ag catalysts can be compared, using the "calibration" curve or, if an adsorption stoichiometry for palladium is accepted, absolute alloy areas can be measured.

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