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NOTES

Ethylene Oxidation Over Supported Silver–Palladium Alloys

The preparation and characterization of supported alloy catalysts poses additional problems to those encountered with supported metals. Some heat treatment may be necessary to alloy the component (supported) metals, but this should preferably not cause extensive crystallite growth and loss of alloy area. There is the need to determine the completeness of alloying achieved and, if possible, any divergence between surface and bulk composition. X-Ray diffraction can provide some information, but the existence of a small amount of unalloyed material, "amorphous" to X-Ray diffraction because of its high dispersion, could entirely alter the catalyst performance and confuse the interpretation of results. Also, the *surface* composition of alloys on supports is not readily accessible to instrumental determination.

In this Note we report a study on supported Ag–Pd alloys that may be usefully compared with work already published on Ag–Pd films prepared by simultaneous evaporation (*1*, *2*). Auger electron spectroscopy shows (*3*) that simultaneous evaporation and annealing up to 400°C produces Ag–Pd alloy films in which the surface and bulk compositions are in close agreement.

The catalytic reaction used was ethylene oxidation, measuring selectivity to ethylene oxide, which changes markedly in the composition range 100% down to 60% Ag. The choice of selectivity as a criterion, rather than specific activity in a simpler reaction, avoids uncertainties associated with reliable surface area measurements in supported alloys. Nevertheless, it appeared advisable to check supported alloy samples of varying composition by electron microscopy for possible crystallite size variation that might introduce unwanted additional effects into the present work. Also, it would be undesirable to have large differences in alloy area leading to widely different conversions, when comparing selectivities at a fixed temperature.

Catalysts were prepared by impregnating the supports with solutions containing silver nitrate and tetramminepalladous nitrate $[(NH_3)_4Pd](NO_3)_2$. Typically, 10 g silica (Davison, grade 70, area 270 m^2/g) was added to 35 ml solution to produce a slurry, and the catalyst dried in an air oven at 40° or 60°C. The alumina support was Alcoa, grade T61 (area 0.04 m^2/g) 10 g was saturated with 7 ml solution and dried at 40°C in air. The metal concentrations in the solutions were adjusted to give metal loadings on the support of 1, 4 or 10% and alloy compositions of 75%–100% Ag. Catalysts were reduced in a flow of pure hydrogen at atmospheric pressure for times and at temperatures specified later.

Catalysts were examined with regard to the extent of alloying achieved by X-ray diffraction using a counter-diffractometer. Where diffraction peaks from a number of crystal planes in the alloy were recorded (in some fired samples), an accurate lattice constant, a_0, was found by extrapolation to $\theta = 90°$ using an appropriate function of the diffraction angle and the centroid position. Lattice constants measured in supported alloy catalysts were compared with a_0 values for bulk Ag–Pd alloys (*4*). Usually only the (111) diffraction peak was recorded and the position of the peak maximum was used, a small correction being made based on the difference between observed and expected a-values in corresponding supported 100% Ag samples. The symmetry of the X-ray diffraction profile is an additional indicator of alloy (bulk) homogeneity. Catalysts were also examined by electron microscopy, using ultramicrotome sections prepared from samples of catalyst set in "Araldite" resin.

Catalysts were tested under flow conditions, with respect to the formation of ethylene oxide as a percentage of ethylene reacted (percent selectivity). A halogen promoter was *not* used, and some attention had to be paid to reactant composition and flow rate to achieve reasonable selectivities under laboratory conditions. A useful selective oxidation occurred over pure silver–silica catalysts (2 g) with a flow of 13.0 ml/min ethylene and 22.5 ml/min oxygen. Alumina-supported catalysts were tested with 5 ml/min each ethylene and oxygen.

Table 1 summarizes X-ray diffraction results on the extent of alloying produced in Ag–Pd alloys supported on silica, at a metal loading of 4%. As a preliminary experiment, catalysts were subjected to treatment A, which involved reduction in hydrogen at 400°C for 2 hr. In one case (90% Ag) there was an indication of a double diffraction peak, but otherwise only single alloy peaks at approximately the correct position were observed. Nevertheless, the peaks were all asymmetrical in shape, giving a clear indication of incomplete alloying. After treatment B, which involved *additional* reduction at 330°C for 18 hr before use as a catalyst for ethylene oxidation, symmetrical peaks were observed in some cases, and lattice constants approached the expected values (mean deviation from expected value, 0.010 Å).

TABLE 1
X-RAY DATA FOR SILICA-SUPPORTED ALLOYS (4% LOADING)

Composition (% Ag)	Lattice constant (Å)			
	Expected	Observed, after various treatments (see text)		
		A	B	C
95	4.074	(4.08)	(4.07)	4.068
90	4.062	(4.09)	(4.06)	4.051
85	4.050	(4.08)	(4.05)	4.040
80	4.039	(4.09)	(4.06)	4.033
75	4.028	(4.02)	(4.03)	4.019

Treatment C involved reducing the dried catalyst at 400°C for 18 hr in the catalytic reactor; an additional overnight reduction at 400°C was also required in the course of experiments to measure selectivity in ethylene oxidation. Catalysts subjected to treatment C gave symmetrical X-ray diffraction peaks, and lattice constants agreed reasonably well with expected values (mean deviation, 0.008 Å). Thus, for catalysts with 4% metal loading, X-ray diffraction indicated that homogeneous solid solutions of Ag–Pd on silica supports had been prepared. However, with 1% metal loadings, no information could be gained because diffraction peaks were not, or were only just detectable.

Figure 1 illustrates the measurements made to characterize the catalysts in terms of selectivity in ethylene oxidation. Catalysts had 1% metal loadings on silica, alloy compositions between 75% and 100% Ag, and had been reduced in the reactor at 400°C for 18 hr (treatment C). Usually a range of temperatures was explored so that the maximum in the selectivity–temperature plot was observed. Similar results were obtained for the catalysts with 4% metal loadings. Much higher selectivity was found with alumina-supported silver (see later), again without the use of any promoter. (It should be noted also that halogen-containing compounds were avoided in catalyst preparation). Under the conditions adopted, the maximum selectivity over pure (silica-supported) silver catalysts fitted in well with the general level of selectivity observed in experiments on pure silver (and Ag–Pd) films on glass (*2*), with which it was proposed to compare the present results. However, it is the variation of selectivity with alloy composition rather than absolute values of selectivity that is under consideration.

This comparison is made in Fig. 2, where the variation in selectivity with composition is shown for Ag–Pd alloys on silica (1% and 4% metal loadings) and for Ag–Pd alloy films. Selectivities are compared at 215°C for supported alloys (conversions were 10%–

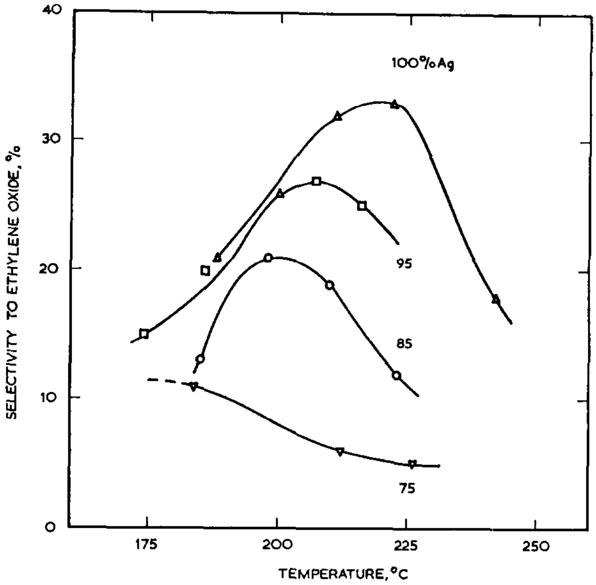

FIG. 1. Selective oxidation of ethylene to ethylene oxide as a function of reaction temperature for Ag and Ag–Pd alloys (composition, percent Ag, indicated) at 1% loadings on silica supports.

20%); reference back to Fig. 1 shows that this choice of temperature clearly reflects the general pattern of selectivity variation with composition. A comparison temperature of 240°C was a suitable choice in experiments with Ag–Pd films, where a static reaction system was used. The transfer of reaction heat (and products) would be expected to have little effect on selectivity in the thin film system. In working with supported alloys, it was found advisable to have small metal loadings.

In both systems, supported alloys and evaporated alloy films, selectivity to ethyl-

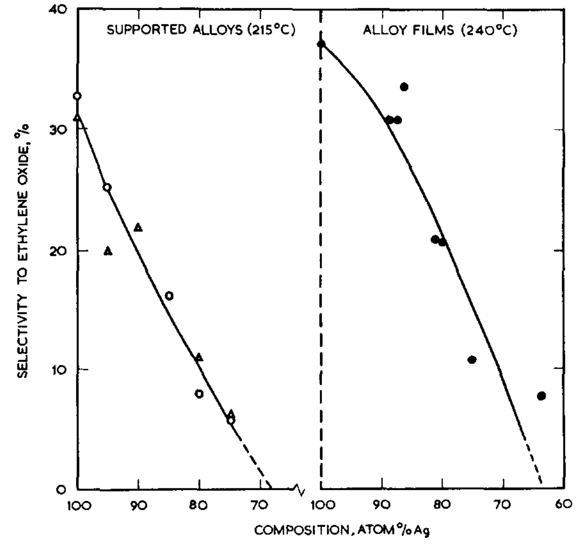

FIG. 2. Selective oxidation of ethylene to ethylene oxide as a function of Ag–Pd alloy composition. Left-hand side: 1% (○) and 4% (△) loading on silica; right-hand side: evaporated films (*2*).

ene oxide formation falls in a similar way with increasing Pd content. The Ag–Pd films had been well characterized by X-ray diffraction with respect to bulk homogeneity (*1*) and, as pointed out above, might also be expected to have identical surface and bulk compositions. Therefore, the test of selectivity in ethylene oxidation as a function of composition suggests that the alloys supported on silica (after treatment C) were also well homogenized, with respect to surface and bulk alloy compositions. The sensitivity of this particular reaction to the presence of unalloyed palladium is shown by the following test. A mixture of 100% Ag-silica and 100% Pd-silica catalysts (4% metal loadings) was prepared to give Ag and Pd in the same proportions as occur in a 95% Ag–5% Pd alloy catalyst, and when this mixture was tested only a trace of ethylene oxide was observed.

If the method for preparing and treating Ag–Pd alloys on silica has produced apparently well-homogenized supported alloys, then it is of interest to examine the dispersion of the alloy crystallites with respect to both size and location on the support. Electron micrographs showed that the alloy crystallites were distributed throughout the silica support structure, with a size range, 30–150 Å, independent of alloy composition from 75% Ag–Pd to 100% Ag.

Because alumina is often thought of as the preferred support for silver to produce ethylene oxide, we examined the degree of alloying and the performance of Ag–Pd on this support (Table 2). Under the conditions used (see experimental methods above), pure silver on alumina (10% loading) showed a maximum selectivity to ethylene oxide of 65%. Heating in air at 500°C for 18 hr, before reduction, only marginally affected this result (72% maximum selectivity). The 95% Ag–Pd on alumina catalyst, after treatment C (hydrogen, 400°C, 18 hr) appeared to be moderately homogeneous. However, in marked contrast to the corresponding silica-supported catalyst, the selectivity decreased to zero for only this 5% Pd addition to silver. Heating in air at 500°C before reduction produced an alloy which, X-ray diffraction indicated, was very well homogenized, but the maximum selectivity was still only 6%.

The pattern is repeated and emphasized by results from the 90% Ag–Pd on alumina catalyst. Now, the standard alloying treatment could produce only a poor alloy showing two separate X-ray diffraction peaks, and the selectivity to ethylene oxide was zero. More vigorous alloying treatment (air, 500°C, 18 hr before reduction) again produced a good alloy, according to X-ray diffraction, but when it was tested as a catalyst, only a trace of ethylene oxide was found.

It could be concluded, therefore, that it is more difficult to bring about alloying when the component metals (as the salts used in the present work) are supported on the alumina as contrasted with the silica support used. Furthermore, while X-ray diffraction may indicate good bulk homogeneity, the sensitive test of selectivity in ethylene oxidation suggested that there was also present "free" palladium or crystallites with palladium-rich surfaces on the alumina support.

TABLE 2

X-RAY AND SELECTIVITY DATA FOR ALUMINA-SUPPORTED ALLOYS

Catalyst		Lattice constant (Å)			Maximum selectivity (%)
% Ag	Treatment (°C)	Expected	Observed	Deviation	
100	H_2, 400° only	—	—	—	65
	Air, 500°; H_2, 400°	—	—	—	72
95	H_2, 400° only	4.074	4.087	+0.013	0
	Air, 500°; H_2, 400°	4.074	4.078	+0.004	6
90	H_2, 400° only	4.062	Separate peaks		0
	Air, 500°; H_2, 400°	4.062	4.068	+0.006	trace

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