JOURNAL OF CATALYSIS 61, 57–65 (1980)

The Structure and Activity of Supported Metal Catalysts

IX. Preparation, Dispersion, and Activity of Palladium–Silver on Silica Catalysts

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Received July 24, 1978; revised May 15, 1979

Techniques were investigated for the preparation of the full range of palladium–silver alloys supported on silica with emphasis on achieving very good (bulk) homogeneity, as determined by the position, symmetry, and shape of X-ray diffraction line-profiles. Gas-phase hydrogen reduction of the impregnated silica was insufficient alone to ensure homogeneity and best conditions for the required high-temperature calcination stage were found. Alternatively, hydrazine reduction in the liquid-phase was followed by heat treatment in nitrogen. The preparative technique adopted, the support area, metal loading, and alloy composition determined the extent of crystallite growth as shown by X-ray line-broadening and electron microscopy. Rates of ethylene hydrogenation as a function of alloy composition were measured for two series of catalysts prepared by calcination + reduction or by hydrazine reduction + heat treatment. Alloying processes and possible barriers to good homogenization are discussed.

INTRODUCTION

Although bimetallic catalysts, sometimes of considerable interest, can be prepared simply by reduction of the mixed salts impregnated on a support, it is also useful to devise techniques for preparing supported catalysts where it can be demonstrated that alloying has been completed, preferably without extensive sintering. The main objective of the present work was to determine if fully homogenized palladium–silver alloys supported on silica could be prepared by a single technique across the composition range. It has been reported that Pd–Ag (on alumina) was alloyed in bulk after annealing at 700°C but silver enrichment of the surface could be detected by Auger electron spectroscopy (*1*). So it was also of interest to discover what hydrogenating activity the present catalysts possessed after the heat treatments found necessary to produce well-homogenized alloys.

EXPERIMENTAL METHODS

Catalysts were prepared from a mixed solution of tetramminepalladous nitrate (Johnson Matthey "Specpure") and silver nitrate ("Analar"). Silica gel (Davison grade 70) was wetted with just more than sufficient solution, evaporated to dryness with stirring on a water bath, and dried overnight in an air oven at 80°C. Catalysts were then calcined, reduced, etc. as discussed later to facilitate alloy formation. Where this involved gas-phase reduction, hydrogen was purified by diffusion through a heated palladium–silver thimble and passed through the catalyst sample at 100 ml/min. Reduction with hydrazine involved stirring a small amount (e.g., 0.1 g) of the dried impregnated silica in 3% v/v hydrazine hydrate solution (e.g., 100 cm^3) at room temperature, standing for an hour, filtering, washing, and drying. In calcination (always in air), the temperature was raised slowly between 80 and 150°C to avoid violent decomposition of the palladium compound. In nitrogen treatments, the sample was purged with nitrogen at room temperature initially.

Ethylene hydrogenation rates were measured in an atmospheric pressure flow system incorporating a narrow U-tube glass reactor (6 mm o.d.) fitted with a side-arm for the exit gas so that a thermocouple

0021-9517/80/010057-09$02.00/0

through a glass joint could be inserted directly into a small bed of catalyst ($\sim$0.1 g). Ethylene (Phillips, Research grade), 5 ml/min, was mixed with hydrogen (purified by diffusion), 100 ml/min, before the reactor. Before testing, the catalyst sample was purged with nitrogen, then hydrogen was passed at room temperature and at 450°C for 2 hr. After reduction the sample was cooled to -100°C in hydrogen and the ethylene flow started. Activity measurements were made at a series of fixed temperatures, analyzing the inlet and outlet composition chromatographically. Arrhenius plots of the data were made from which the conversion at the chosen comparison temperature was obtained.

Alloy dispersion was estimated from apparent crystallite sizes determined by X-ray line-broadening and from electron micrographs of ultramicrotome sections. An account of the procedures used for both these and CO chemisorption measurements, when applied to supported metal catalysts, is given elsewhere (*2*).

RESULTS

The extent of alloying was determined by a careful examination of the X-ray diffraction line-profiles with respect to their position, symmetry, and shape. Thus the lattice constant derived from the position of the diffraction peak should correspond closely to that predicted from a knowledge of the alloy composition and the lattice constants of bulk alloys (*3*). Obviously asymmetrical diffraction peaks are a good indicator that the homogenization treatment was insufficient and, in extreme cases, very irregular or even separate peaks may be observed.

In preliminary experiments attempts were made to apply across the full composition range the different types of homogenizing treatment used previously with partial ranges of silica-supported Pd–Ag, i.e., reduction at 400°C of 0–25% Pd–Ag (*4*) and calcination + reduction at 400°C of 50–100% Pd–Ag (*5*). When applied to the 50% Pd–Ag samples, in the present work, "reduction only" was an unsatisfactory homogenizing treatment even at 600°C (Table 1), yielding irregular X-ray diffraction profiles tending to separate into component peaks. Treatments involving "calcination + reduction" of 50% Pd–Ag samples at 400°C (Table 1) and higher temperatures, 450°C, 500°C, and (also shown in Table 1) 600°C were usually also unsatisfactory. After calcination + reduction at 750°C, the X-ray profile still showed asymmetry ("asym.")

TABLE 1

Alloying by Calcination and Reduction (4% Loading on Standard Silica)

Composition (atom% Pd)	Calcination temperature[a] (°C)	Reduction temperature[b] (°C)	Lattice constant (Å)	Peak shape	Calculated composition[c] (atom% Pd)
50	—	600[d]	3.975	Irregular	52
50	400	400	3.945	Irregular	68
50	600	600	3.945–3.995[e]	Asym.	42–68
50	750	750	3.975	Asym.	52
25	600	600	4.035	Asym.	22
25	800	800	4.034	$\sim$Sym.	23
75	600	600	3.929	$\sim$Sym.	78
75	750	750	3.926	V. Asym.	79

[a] Three hours (air).

[b] Two hours (H_2), unless otherwise stated.

[c] From lattice constant.

[d] Five hours.

[e] Five results.

but the sample had almost the correct lattice constant, corresponding to a composition of 52%.

High-temperature calcination + reduction at 600 or 800°C applied to 25% Pd–Ag samples (Table 1) yielded approximately correct lattice constants, but whereas after treatments at 800°C, the X-ray profile was nearly symmetrical ("sym.") some asymmetry was observed after treatments at 600°C. To complete this first series of measurements, samples with 75% Pd were also homogenized by calcination + reduction. As expected, the lattice constants measured, 3.929 and 3.926 Å, were close to the correct value (3.933 Å), but the sample treated at 750°C yielded an X-ray profile of poor shape, although the symmetry was satisfactory after treatment of the sample at 600°C.

It was apparent from the above work that homogenization by calcination + reduction required temperatures near the collapse temperature of the silica pore structure. When samples of Davison "70" silica were heated for 5 hr (the total treatment time for the samples listed in Table 1) at 650, 750, and 800°C, the measured surface areas were 287, 282, and 205 m^2/g, respectively. Extending the heating period at 800°C to 16 hr decreased the surface area substantially, to 15.5 m^2/g. Accordingly, further series of Pd–Ag alloys were prepared (4% loadings) containing 25, 50, or 75% Pd on *prefired* silica (800°C for 16 hr; surface area 15.5 m^2/g), as shown in Table 2.

Calcination + reduction at 600°C was now sufficient to produce a reasonably good alloy at the 50% Pd composition, but less satisfactory alloys containing 25 and 75% Pd. *Calcination at 800°C + reduction at 450°C proved to be the best set of conditions* among those investigated for homogenizing Pd–Ag alloys by the calcination + reduction method. After this treatment, 25 and 50% alloys were apparently nearly perfect and a reasonably good 75% Pd alloy was produced (Fig. 1A).

At this stage of the investigation it had been recognized that the 75% Pd composition was difficult to homogenize consistently to the nearly perfect alloy. Thus when both calcination and reduction temperatures were carried out at 800°C, the 25 and 50% Pd alloys were again entirely satisfactory but the 75% Pd alloy yielded a flattened asymmetric X-ray profile. High-temperature reduction alone (last result,

TABLE 2

Alloying by Calcination and Reduction (4% Loading on Prefired Silica)

Composition (atom% Pd)	Calcination temperature[a] (°C)	Reduction temperature[b] (°C)	Lattice constant (Å)	Peak shape	Calculated composition[c] (atom% Pd)
25	600	600	4.029	Asym.	25
50	600	600	3.973	Sym.	53
75	600	600	3.940	Asym.	71
25	800	450	4.027	Sym.	26
50	800	450	3.980	Sym.	50
75	800	450	3.934	~Sym.	75
25	800	800	4.028	Sym.	25
50	800	800	3.978	Sym.	50
75	800	800	3.941	Asym.	70
75	—	800[d]	—	Two Peaks	—

[a] Three hours (air).

[b] Two hours (H_2), unless otherwise stated.

[c] From lattice constant.

[d] Five hours.

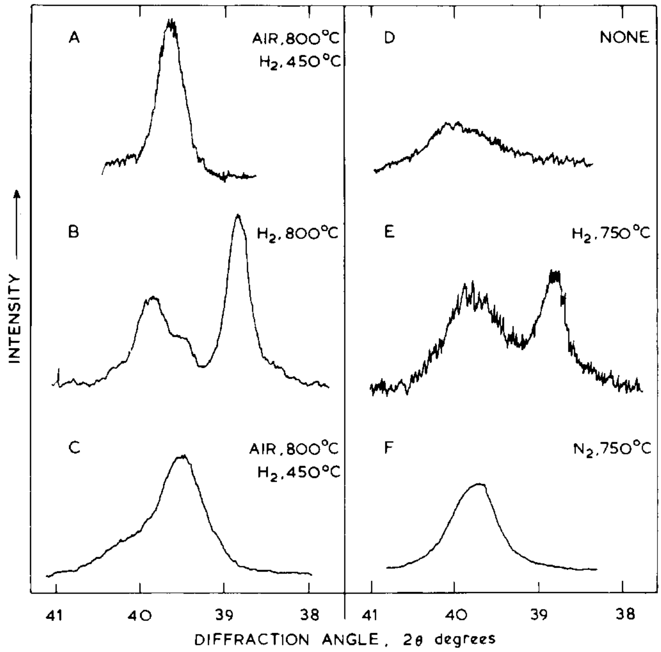

FIG. 1. X-Ray diffraction profiles of 75% Pd–Ag/silica catalysts. (A)–(C), prepared by calcination in air, and/or by reduction in gas-phase hydrogen: (A), (B), 4% loading on prefired silica, (C) 10% loading on standard silica, (D)–(F), 10% loadings on standard silica, prepared by hydrazine reduction: (D) without further heat treatment, (E), (F) heat treatment as indicated.

Table 2) was completely unsatisfactory yielding a twin-peaked profile. Hydrogen dissolution was considered but the result was unchanged by overnight outgassing at 450°C (Fig. 1B). Alternatively, 75% Pd catalysts were reduced in hydrazine hydrate solution at room temperature (as described under Experimental Methods) using 10% metal loadings on *unfired* silica. Figures 1D, E, and F show clearly that a subsequent heat treatment in *nitrogen* was required to achieve reasonable homogenization.

Alloy Dispersion

It is of interest to determine the extent of crystallite growth caused by the severe heat treatments employed and Fig. 2 shows *apparent* crystallite size determined by X-ray line-broadening. Profiles may be broadened by the occurrence of both small crystallites and by inhomogeneities within crystallites or differences in crystallite compositions. It would seem that the actual sizes of the alloy crystallites should lie between the sizes determined for pure silver and pure palladium and (relating inversely to the melting point) the size should decrease from pure silver to pure palladium. The upper plot (Fig. 2, open circles) shows mean apparent crystallite sizes from three sets of catalysts with 4% metal loadings on prefired silica (7–15 m^2/g surface area) where homogenization was produced by calcination at 800°C + reduction at 450°C. The variation of apparent crystallite size with composition followed the expected behavior and therefore suggests that *actual* crystallite sizes had been measured. The actual sizes ranging from 515 Å (pure silver) down to 260 Å (pure palladium) are, of course, very much larger than for a typical supported metal catalyst.

Although some penalty for achieving reasonable alloy homogeneity seems inevitable, rather better alloy dispersion should be possible. For example, 10% metal loadings on unroasted silica used for catalytic measurements prepared by calcination (800°C) + reduction (450°C) were reasonably ho-

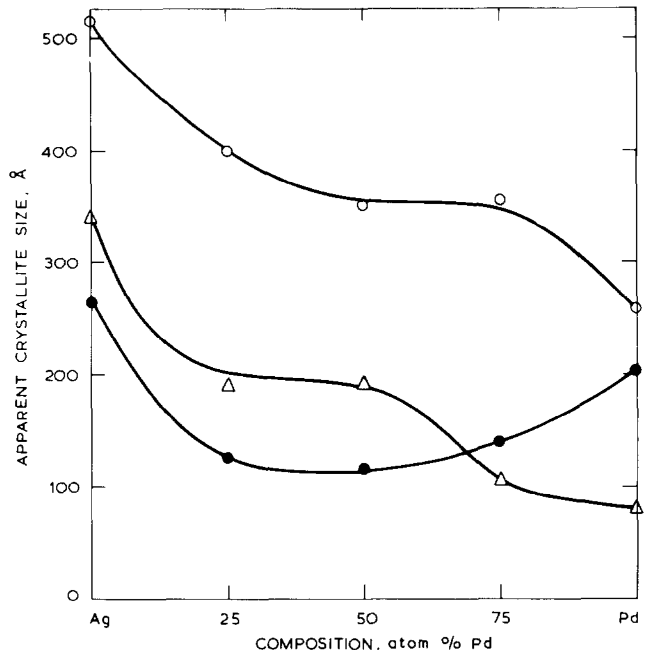

FIG. 2. Variation of apparent crystallite size with alloy composition for 4% alloy loadings on prefired silica (○) and 10% loadings on unroasted silica (△), both prepared by calcination at 800°C + reduction at 450°C, and for 10% loadings alloyed by hydrazine reduction + heat treatment (●).

mogeneous and contained crystallites ranging from 340 Å mean size (pure silver) to 80 Å (pure palladium). The apparent mean crystallite sizes of the alloys (Fig. 2, triangles) changed progressively between these values. Presumably some resistance to sintering is conferred by the higher area (unroasted) support. The crystallite size ranges observed in electron micrographs of these latter catalysts were 50–250 Å (pure Pd), 50–500 Å (75% Pd–Ag), and 50–300 Å (50% Pd–Ag). Thus the mean crystallite size determined by X-ray line-broadening (Fig. 2, triangles) for the 75% Pd–Ag samples, i.e., ~100 Å, may be too small, due to alloy inhomogeneities. The electron micrographs suggest that the actual mean size for the 75% Pd–Ag alloy was at least equal to the value obtained for the 50% Pd–Ag alloy by line-broadening, i.e., ~200 Å.

Alloys formed by hydrazine reduction + heat treatment at 750°C (15 hr) *appear* to have still smaller crystallites (Fig. 2, filled circles), but the comparison with the pure metals suggests some contribution to line-broadening from alloy inhomogeneity and, indeed, some profile asymmetry was evident in the 50% alloy. Electron micrographs of catalysts prepared by hydrazine reduction + heat treatment and containing 10% metal showed the following size ranges: 100–300 Å (pure Pd), 60–300 Å (75% Pd–Ag), and 60–400 Å (50% Pd–Ag). In general, electron micrographs of such catalysts also seemed to contain many fewer crystallites per unit area than catalysts prepared by calcination + reduction.

Catalytic Activity

The catalysts prepared on prefired silica, although very well homogenized, had poor hydrogenating activity, e.g., for benzene hydrogenation. However, it was found that 10% loadings on unroasted silica, despite the calcination + reduction needed to homogenize them, were satisfactory catalysts (Table 3) for ethylene hydrogenation, being active down to about −70°C or lower. Figure 1C illustrates the homogeneity achieved on the standard silica, for

TABLE 3

Dispersion and Activity of Pd–Ag/Silica Catalysts (10% Loading on Standard Silica)

Preparative method	Composition (atom% Pd)	X-ray data			CO adsorption (ml/g cat)	C_2H_4 converted (%) at −73°C
		Lattice constant (Å)	Peak shape	Crystallite size[a] (Å)		
Calcination	100	3.888	Sym.	90	0.6	31.6
+	75	3.930	Asym.	105	0.1	7.2
Reduction[b]	50	3.981	~Sym.	210	0.02	0.6
Hydrazine reduction	100	3.883	Sym.	280	0.1	1.5
+	75	3.926–3.949[d]	~Sym.	165	0.05	0.3
Heat treatment[c]	50	3.989	~Sym.	115	0.0	0.04

[a] Values for alloys are apparent crystallite sizes.

[b] Calcination (800°C, 3 hr); reduction (450°C, 2 hr).

[c] Heat treatment (750°C, N_2, 15 hr).

[d] Five results.

the 75% Pd–Ag composition, examined after use as a catalyst. The profile shows some asymmetry but the composition calculated from the lattice constant at 77% Pd–Ag was close to the expected value.

Alloys formed by hydrazine reduction + heat treatment were less active for ethylene hydrogenation than alloys prepared by calcination + reduction (Table 3). The variation of reaction rate with composition is shown in Fig. 3. Reaction rates were determined from Arrhenius plots and a higher comparison temperature (−23°C) was chosen for the hydrazine reduced catalysts be-

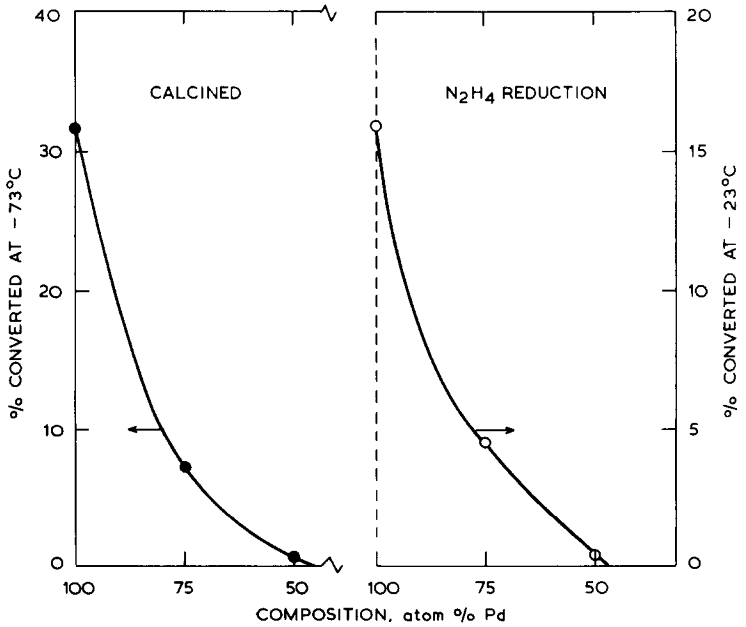

FIG. 3. Variation of ethylene hydrogenation rate with alloy composition for catalysts with 10% metal loadings on standard silica, either (left-hand side) calcined in air at 800°C, reduced at 450°C or (right-hand side), reduced with hydrazine and heated in nitrogen (750°C, 15 hr).

cause of their lower activity, to improve accuracy. Although the general level of activity was different for the two types of catalyst, nevertheless the pattern of activity variation with composition was the same in each case.

DISCUSSION

It has been shown for the specific Pd–Ag/silica system studied that reduction alone by dry gas-phase hydrogen even at 600°C (50% Pd–Ag on standard silica) or 800°C (75% Pd–Ag on pre-fired silica) was a very inadequate alloying technique. A severe calcination stage was needed which may require the use of a prefired silica support. Using prefired silica and 4% alloy loadings, calcination at 800°C, followed by reduction at 450°C, proved to be the best conditions for producing the full range of Pd–Ag alloys with very good (bulk) homogeneity. However, the 75% Pd–Ag composition was difficult to homogenize consistently well (and presumably this applies to compositions around 75% Pd–Ag). Alternatively the metal compounds impregnated on the support may be reduced in the liquid-phase by hydrazine and alloying completed by heat treatment at 750°C in nitrogen (but not hydrogen).

It would appear that barriers to good homogenization may occur at various process steps: (i) mixed metal salt crystallites may have a reasonably uniform composition but on reduction the palladium and silver atoms still have to be randomized; (ii) the crystallites deposited on the support by the initial impregnation may vary greatly in composition, the salts crystallizing separately in the extreme case. The effect of the various alloying treatments on these processes might be briefly considered.

Process (i), i.e., randomization, should not be difficult at the temperatures/times used. Information on the diffusion coefficients (D) for palladium and silver in Pd–Ag alloys has been used previously to interpret conditions necessary for homogenizing Pd–Ag films (*6*). Further data are now available on the variation with composition of D_{Pd} (*7*) as well as D_{Ag} for alloys with up to ~20% Pd, viz.,

$$D_{\mathrm{Pd}} = 12.5 \exp(-7.5\,X) \exp(-57{,}200/RT) \quad (1)$$

$$D_{\mathrm{Ag}} = 0.270 \exp(-8.2\,X) \exp(-43{,}700/RT) \quad (2)$$

where X is the atom fraction of palladium. These equations show the higher activation energy (cal mole^{-1}) associated with D_{Pd} and also the strong dependence of the diffusion coefficients on alloy composition. Because of the latter feature, it was suggested (again with respect to alloy films) that it is best to calculate the RMS interdiffusion distance, L, for diffusion normal to the interface between two pure components (*8*). For interdiffusion in the Pd–Ag system after heating for 1 hr at 300 or 400°C, the values of L are 21 and 110 Å, respectively, using volume interdiffusion data from Neukam (*9*). The bulk diffusion data can only be regarded as an approximate guide but they do suggest the need for temperatures above 400°C to randomize the atoms and also, as found, the greater difficulty of alloying Pd-rich compositions.

Considering process step (ii), it would appear that once salt crystallites of different compositions have been deposited, then extensive material movement will be needed to produce a good alloy eventually. Although most results refer to platinum, it seems that crystallite growth is more extensive in oxygen rather than hydrogen or nitrogen atmospheres, providing some justification for the calcination stage prior to catalyst reduction to promote material movement. However, palladium forms a bulk tetragonal oxide PdO above 400°C which is stable in air to 700°C whereas silver oxide is unstable above 300°C. There is strong adhesion between PdO and SiO_2 (*10*) and while PdO persists, successful alloying may be inhibited by the stronger interaction between oxides than between metal and oxide (i.e., silver and SiO_2 or

PdO) so that silver tends to agglomerate rather than interdiffuse with PdO. It may be significant that the calcination temperature found suitable, 800°C, was above the apparent decomposition temperature of PdO.

With respect to the apparent inhomogeneities still existing after high-temperature treatment, 600–800°C, in a reducing atmosphere, then interaction between palladium and the support may be responsible. It has been reported elsewhere (*11*) for Pd/silica catalysts (similarly prepared from the starting materials used here) that raising the reduction temperature to 600°C caused metal–support interaction. Extra X-ray diffraction lines appeared which could be removed again by calcination at 800°C (+ reduction at 450°C). It was suggested that the palladium-aided reduction of silica is followed by the formation of a palladium–silicon intermetallic compound, although this could not be convincingly indexed with data in the JCPDS file. Whatever the nature of this interaction of palladium with the support, it would seem counterproductive to the necessary material movement needed to form homogeneous alloy crystallites starting from salt crystallites of nonuniform composition. Liquid-phase reduction using hydazine solution may be beneficial if the salt crystallites dried out on the support are nonuniform in composition. The reduced metals may be redeposited from solution in the pores of the support and the subsequent heat-treatment using nitrogen (rather than gaseous hydrogen) produces reasonably well homogenized alloys.

Catalytic Activity

Activity decreased when silver was added, falling from maximum values over 100% Pd catalysts to very low rates over the 50% alloys. The capacity for CO chemisorption also fell with increasing silver content and to a greater extent than indicated by the changes in dispersion (see also under Alloy Dispersion for crystallite sizes in electron micrographs), again indicating the presence of silver at the alloy surfaces. The variation of ethylene hydrogenation rate as a function of *surface* composition is as yet unknown so the activity pattern observed in the present work cannot be used to assess the effect of preparation on surface enrichment. It would seem, however, that silver has not totally obscured the surface of 75% and even 50% Pd–Ag alloys, because of the activity which they exhibit. Over hydrogen-pretreated Pd–Ag ribbons at 100°C (*12*), ethylene hydrogenation rates passed through a maximum at ~65% Pd–Ag and then decreased to zero at ~35% Pd–Ag. The activity maximum was correlated with hydrogen solubility which is always a possible complication with palladium-based alloy catalysts leading to apparent activity enhancements if pure palladium is poisoned. No enhancement was observed in the present work where much lower reaction temperatures were used.

The ethylene conversion rate was markedly lower over catalysts prepared by hydrazine reduction + heat treatments compared with calcined and reduced catalysts. In part this difference was due to lower dispersion, e.g., comparing the pure palladium catalysts, the crystallite size was three times larger and the CO chemisorption capacity six times smaller, whereas the conversion rate was about 20 times lower. It is known that the silica support used contains traces of iron and sulfate which decrease the hydrogenating activity of palladium (*13*), and the different alloying methods used in the present work may have varied their concentrations in the finished catalyst, e.g., burning off the sulfur during calcination. Alternatively, the differences in (specific) activity may be associated with the relatively small number of crystallites usually visible in electron micrographs of catalysts prepared by hydrazine reduction + heat treatment.

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