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NOTE

# Hydrogen Chemisorption and Phase Composition of Silica-Supported Rhodium–Silver Alloys

## INTRODUCTION

We have recently reported that the surface composition of platinum–copper crystallites supported on silica gel is a function of alloy crystallite size and can differ from the composition of the interior of the crystallites (*1*). This note reports similar work in the rhodium–silver system. This alloy system was chosen because, unlike platinum and copper, rhodium and silver are not expected to form solid solutions or intermetallic compounds. Hence, it is of interest to see whether either of these metals is preferentially segregated to the surface of the other.

## EXPERIMENTAL WORK

The alloys were prepared by impregnation of Davison grade 62 silica gel (surface area = 340 $m^2/g$, pore vol = 1.15 $cm^3/g$) with a rhodium chloride solution followed by impregnation with a solution of silver nitrate. The total metal loading was 5% of the weight of the dry support. The order of impregnations or drying between impregnations did not seriously alter the metal distribution on the finished catalyst. After impregnation with both solutions, the catalyst was dried over night in a vacuum at 120°C. The dried catalysts were reduced in flowing hydrogen at 480°C for 2 hr.

The reduced catalysts were examined by X-ray diffraction using a Norelco Diffractometer with Cu $K\alpha$ radiation. Pure silver and pure rhodium were found in all samples. The lattice parameters found for silver and rhodium on the catalysts agree well with published values (see Table 1) indicating very little solid solubility of the metals. This is in agreement with the rhodium–silver phase diagram (*2*).

The silver and rhodium crystallite sizes were estimated from the broadening of the (111) X-ray diffraction line using the Scherrer equation (*3*). The metal surface area was calculated from the crystallite sizes assuming the crystallites to be spherical and not in contact (see Table 2). Hydrogen chemisorption by all alloys was measured at 0°C in a flow apparatus using a mixture of 1% hydrogen in Argon (*4*). In Fig. 1, the measured hydrogen chemisorption divided by the total metal surface area is plotted against the fraction of the total surface which is due to rhodium crystallites.

TABLE 1
OBSERVED LATTICE PARAMETERS OF RHODIUM–SILVER ALLOYS

| Alloy composition (wt % Ag) | Lattice parameter (Å) | |
|---|---|---|
| | Rhodium[a] | Silver[a] |
| Pure Rh | 3.826 ± 0.004 | — |
| 20 | 3.830 ± 0.004 | 4.087 ± 0.004 |
| 50 | 3.829 ± 0.01 | 4.089 ± 0.004 |
| 50 | 3.812 ± 0.01 | 4.087 ± 0.004 |
| 80 | — | 4.091 ± 0.004 |
| Published values for the metals[b] | 3.804 | 4.086 |

[a] The uncertainties listed reflect the precision of the measurements and include consideration of the reproducibility of the instrument and uncertainty in locating the maximum of the diffraction peak.

[b] "Handbook of Metals," p. 51 American Society for Metals, Novelty, Ohio (1961).

TABLE 2
Crystallite Size and Surface Area of Rhodium–Silver Alloys

| | Rhodium[a] | | | Silver[a] | | |
|---|---|---|---|---|---|---|
| Alloy composition (wt. % Ag) | Crystallite size (Å) | Surface area ($m^2/g$) | No. of Rh crystals/g of catalyst | Crystallite size (Å) | Surface area ($m^2/g$) | No. of Ag crystals/g of catalyst |
| Pure Rh | 40 ± 4 | 6.0 | — | — | — | — |
| 20 | 48 ± 5 | 4.0 | $6 \times 10^{16}$ | 370 ± 80 | 0.15 | $3 \times 10^{13}$ |
| 50 | 57 ± 6 | 2.1 | $2 \times 10^{16}$ | 260 ± 50 | 0.55 | $3 \times 10^{14}$ |
| 50 | 69 ± 6 | 1.7 | $1 \times 10^{16}$ | 670 ± 200 | 0.21 | $2 \times 10^{13}$ |
| 80 | — | ~1[b] | $\sim 1 \times 10^{16}$ | 670 ± 200 | 0.34 | $2 \times 10^{13}$ |

[a] The probable errors which are listed are estimates of the incertainty in making the line broadening measurements and of making the instrumental broadening correction.

[b] Estimated from the crystallite size observed on other catalysts.

## Discussion

The observed chemisorption of alloys containing 10% or more silver is much less than expected from the rhodium surface area as calculated from the X-ray diffraction pattern. There are several possible explanations for this. First, contrary to the assumption made above, the crystallites of rhodium and silver may be in contact, reducing the free rhodium surface. The observed reduction in rhodium surface requires that the rhodium crystallites be surrounded by silver crystallites. This is unlikely, however, because the number of rhodium crystallites is much larger than the number of silver crystallites (see Table 2).

Alternatively, each crystallite may consist of two phases and the smaller rhodium crystallites may be imbedded in the larger silver crystallites. This has been observed in the copper–nickel system (*5*). Table 2 shows that, if this were true, approximately 300 to 1000 rhodium crystals would have to be imbedded in each silver crystal. This is not likely because the relative size of the crystals would require unreasonably tight packing of the rhodium crystallites inside the silver crystallites.

Finally, it is possible that there might be a layer of silver a few atoms thick on each rhodium crystallite. This behavior is found in larger (>50 Å) crystallites of platinum-copper alloys (*1*). Complete coverage of the rhodium by a monolayer of silver would use only a small fraction (about 10%) of the silver atoms present. This explanation seems most likely at present. These experiments suggest how catalyst activity may be related to the phase structure and surface composition of supported metals when more than one metal is present.

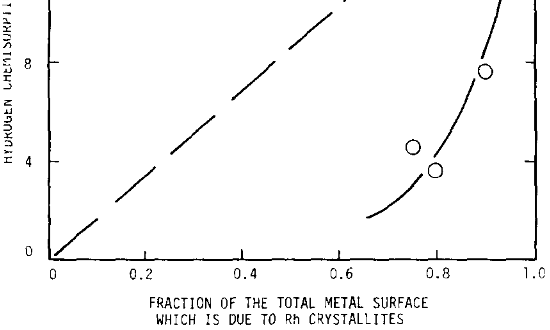

Fig. 1. Hydrogen chemisorption as a function of the fraction of the surface which is due to rhodium crystallites: broken line, expected curve for no Rh–Ag interaction.

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