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Olefin Hydrogenation Catalyzed by Supported and Unsupported Mixed Metals*

S. H. INAMI AND H. WISE

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

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The results of a series of measurements are reported on the hydrogenation activity of the catalyst system: palladium–gold. Two types of catalysts are employed, one in the form of metal microspheres containing different compositions of the two metals as alloys, the other in the form of the mixed metals dispersed on an alpha-alumina support. The alloy-microsphere system exhibits a pronounced increase in specific activity for cyclopentane hydrogenation at 500°K resulting from the addition of gold to palladium with a maximum near 50 at.% gold. On the other hand the supported mixed-metal system exhibits an entirely different pattern in specific activity for benzene hydrogenation at 473°K. It is concluded that although X-ray data and electron microprobe analysis indicate alloy formation for the supported catalyst, the surface phase of the crystallites is not in composition equilibrium with the bulk in spite of the fact that the Pd–Au system exhibits complete miscibility over the entire range of compositions.

INTRODUCTION

The inquiry into the relationship between the electronic configuration of metals and their catalytic activity has led to a number of investigations on the catalytic properties of metal alloys. Especially mixtures of metals composed of the elements of Groups VIII and IB have been studied, and in a number of catalytic hydrogenations of unsaturated compounds, increases in specific activity have been reported with addition of IB-metal up to a maximum of 30–50 at.% (*1*). This pattern in activity is observed on nickel–copper catalysts during the hydrogenation of acetylene (*2*) and of benzene (*3*), on palladium–silver catalysts during the hydrogenation of ethylene (*4*), and on palladium–gold catalysts during the *ortho–para* hydrogen conversion (*5*). In the last case, the kinetic data exhibit a region of constant activation energy but variable rate coefficient due to changes in the preexponential factor of the Arrhenius expression. These results have been interpreted in terms of electron promotion to a localized band as gold is added to palladium, thereby altering the availability of electronic energy levels and affecting the activation entropy of the system (*6*). Recent studies by Sachtler and coworkers on the surface composition of Ni–Cu (*7, 8*) and Pt–Au (*9*) alloy films have indicated that under certain conditions, phase separation may occur due to the existence of a miscibility gap and to differences in the diffusional transport coefficients of the components of the binary metal system. As expected, the catalytic properties of such metal films did not exhibit the characteristics observed for metal alloys prepared at high temperatures and quenched to the reaction temperature, thereby "freezing in" the bulk alloy structure (*10*).

Of special interest to catalyst technology is the development of a supported catalyst containing small metal alloy particles dis-

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persed on high surface-area carriers. In selecting the metal components for such a study, the Pd–Au system offers the advantage of a complete range of solid solubility. Thermodynamic data indicate that the enthalpies of formation as a function of composition remain negative over the entire composition range (*11*). However, it remains to be seen whether the surface compositions of metal crystallites formed on a support differ from that of the bulk alloy due to differences in surface free energies of the two metal components in the solid solution. In the following study of olefin hydrogenation, a comparison is made of the catalytic properties of Pd–Au alloys in the form of bulk metals (microspheres, particle diameters ~50 μm) and in the form of dispersed crystallites (particle diameters <1000 Å).

Experimental Details

A. *Palladium–Gold Microspheres*

For the unsupported Pd–Au microspheres,† a microreactor system (*12*) was designed with gas flow rates adjusted to permit relatively short contact times between the catalyst and the gas mixture. The prepurified hydrogen carrier gas (flow rate of 65 cc/min at 14 psig) flowed through a three-way injection valve and thence through the catalyst bed contained in a glass reactor to the gas chromatographic apparatus. The cyclopentene reactant kept at ice-bath temperature (partial pressure of about 100 Torr) was entrained in a second hydrogen stream which flowed through a sample loop (volume 1.5 cc) connected to the injection valve. When desired, the main carrier gas could be diverted to sweep the reactants contained in the loop into the reactor. The reacted gas mixture was analyzed by means of gas chromatography with a 10-ft column of bismethoxyethyl adipate supported on Chromosorb W, and thermistors as detectors.

To remove carbon-containing adsorbates, the alloy microspheres (diam. 44–53 μm) were first exposed to an atmosphere of oxygen at 570°K for 3 hr. A small quantity (10 to 20 mg) of the spheres, diluted with 1.5 g of aluminum oxide,‡ was then placed in the glass reactor. The catalyst was pretreated with hydrogen at 500°K for approximately 2–3 hr preceding the experimental measurements, which were carried out at the same temperature. As tested in a separate experiment, aluminum oxide was found to be inert for the hydrogenation reaction under these conditions. A new glass reactor was used for each alloy composition to avoid the possibility of trace quantities of catalyst remaining from previous experiments. The lattice spacings of these alloys as a function of gold content were determined by X-ray diffraction technique. The spacings were in excellent agreement with published X-ray data (*13*, *14*).

For determination of the surface area of the metal-alloy microspheres by the BET method, a special apparatus was constructed§ for krypton adsorption measurement of low-area bulk metal samples (*15*). Using a thermistor pressure gage incorporated into an electrical bridge circuit and working in the pressure range from 1 to 500 μm with a dead space of 7 cc, we were able to determine adsorbed gas volumes as small as 1×10^{-3} cc (STP) with a precision of ±3%. The surface areas so determined for the various alloy catalysts are presented in Table 1.

B. *Supported Palladium–Gold Catalysts*

The catalysts used in this phase of the investigation were prepared by conventional impregnation techniques. Palladium and gold foils were dissolved in *aqua regia* to

TABLE 1
Surface Area of Microsphere Alloy Catalysts

Composition of catalyst (at.% Au)	Surface area (cm^2/g)
0	139
40	102
60	110
100	85

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† Supplied by Engelhard Industries, Newark, N.J.

‡ Reagent grade (Merck & Co.).

§ These measurements were carried out by Dr. H. L. Gruber.

make up solutions containing 5 wt % of metal. Measured aliquots of these solutions were used to impregnate an alumina carrier¶ (65% alpha, surface area 20 m^2/g). The catalyst contained 2.2 wt % metal (relative to suport) or the gram-atom equivalent thereof as alloy. A series of Pd/Au catalysts was so prepared, containing 0, 20, 40, 60, 80, and 100 at.% gold. The impregnated powders were dried in air at 125°C, then reduced in a stream of hydrogen (1 atm pressure) first at 400°C for 4 hr, then at 700°C for 4 hr.

For X-ray diffraction analysis, the powders were heated at 500°C under vacuum to remove dissolved hydrogen, which is known to cause changes in the lattice spacing of the metal (*13*). The results of the X-ray analyses for these samples indicated formation of alloys having poorly defined compositions. Subsequently, the catalyst samples were given a second 2-hr treatment at 900°C under vacuum. Following this treatment, X-ray analysis of the catalysts showed that the Pd–Au mixtures had alloyed completely, each mixture exhibiting a single definite composition (Table 2).** The X-ray lattice parameters of the supported catalysts with pure gold and the pure palladium were found to be in excellent agreement with data of Maeland and Flanagan for the unsupported metals (*14*).

TABLE 2
X-RAY ANALYSIS OF SUPPORTED CATALYSTS

Nominal composition[a] (at.% Pd)	Composition from X-ray analysis (at.% Pd)
100	100 ± 5
80	75 ± 5
60	54 ± 5
40	38 ± 5
20	22 ± 5
0	0

[a] Corresponding to atomic ratios of palladium and gold in the solution used in impregnating the porous support.

The catalytic efficiencies of these catalysts as a function of alloy composition were examined in the hydrogenation of benzene at 473°K. In a typical experiment, 100 mg of supported catalyst diluted with one gram of inert Al_2O_3 (same as used for the support) was placed in a glass reactor and pretreated in a stream of hydrogen for several hours at 200°C. A feed stock comprising a 1/25 mole ratio of benzene to hydrogen was allowed to flow continuously (flow rate of 25 cc/min at one atm) over the catalyst, and product gases were analyzed at suitable intervals by gas chromatography. The catalysts were found to be catalytically stable for several hours during the course of the experiments.

For the determination of the surface area of these supported alloys, chemisorption of CO was employed (*16*). A Cahn microbalance* was incorporated into a vacuum system. About 0.5 g of supported catalyst was placed on the aluminum pan, which was suspended from the beam of the balance by a quartz fiber. The catalyst was degassed at 400°C for approximately 15 hr under vacuum; it was then cooled to room temperature and 25 Torr of CO was introduced into the system. A molecular sieve trap was employed to remove traces of CO_2 from the CO supplied with a purity specification of 99.5% by volume. The microbalance continuously recorded the mass change associated with the uptake of CO. After sorption equilibrium had been reached, which required from 1 to 2 hr, the physisorbed CO was pumped off the sample at room temperature. The quality of chemisorbed CO was found from the difference in mass between the physisorbed portion and the total mass adsorbed. The process was repeated with successively higher pressures of CO until the weight change due to chemisorption reached a limiting value as a function of CO pressure. The metal surface area was calculated by assuming a value of

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¶ Kaiser Aluminum & Chemical Corp.

** Similarly electron-microprobe analysis on several of these samples indicated metal compositions expected on the basis of the preparative procedure. (We are indebted to Dr. H. Harnsberger of Chevron Research Corporation for these analyses).

* Cahn Instrument Company, Paramount, CA.

0.86×10^{15} surface sites for CO adsorption per cm^2 of Pd or Pd–Au alloy surface. In a blank run, the chemisorption of CO on the support, Al_2O_3, prepared in the same manner as the other catalysts, was carried out. The uptake of CO by Al_2O_3 was found to be small (10 ± 10 μg) and within the limits of precision of the measurement. Therefore, the contribution of CO sorption on Al_2O_3 was neglected in the surface area determination of the supported catalyst.

EXPERIMENTAL RESULTS

A. *Palladium–Gold Microspheres*

The experimental results obtained for cyclopentene hydrogenation as a function of alloy composition are shown in Table 3. The specific conversion (% conversion/cm^2 surface area) is based on the analyzed composition of the product gas mixture and the measured surface area, for each catalyst employed. In a series of five or more determinations, the reproducibility of the total conversion data for each catalyst was found to be within ±8%. It is of interest to note that a marked increase in catalytic hydrogenation activity is observed for alloys containing up to 60 at.% gold over that measured for pure palladium.

B. *Supported Palladium–Gold Catalysts*

Since cyclopentene hydrogenation was too rapid over the supported Pd–Au catalyst (even at room temperature), benzene was substituted for the olefin in these measurements. The experimental results are summarized in Table 4. The specific conversion (relative to palladium) exhibits initially a rise in activity as gold is added to the catalyst, but further addition of IB metal brings about a pronounced activity decrease. This pattern is entirely different from that observed with the Pd–Au microspheres.

TABLE 3
HYDROGENATION OF CYCLOPENTENE OVER Pd–Au MICROSPHERES AT 500°K

Catalyst composition (at.%)		Specific conversion relative to Pd
Pd	Au	
100	0	1.00
80	20	1.10
60	40	1.74
40	60	1.77

TABLE 4
HYDROGENATION OF BENZENE OVER SUPPORTED Pd–Au CATALYSTS AT 473°K

Catalyst composition (at.%)		Surface area[a] (m^2/g)	Specific conversion relative to Pd
Pd	Au		
100	0	0.44	1.00
75	25	0.42	1.24
54	46	0.68	0.64
38	62	1.25	0.16
22	78	0.30	0.04

[a] CO sorption.

DISCUSSION

The experimental results for the Pd–Au microspheres offer further evidence on the enhancement of catalytic hydrogenation activity brought about by the addition of Group IB metal to a Group VIII metal. There is no indication that for the Pd–Au alloy system the filling of the *d* band at 60 at.% introduces a sharp change in the activity pattern, an observation which applies as well to other alloy systems studied, such as Pd–Ag (*4*). As discussed in an earlier publication (*6*), the catalytic data may reflect certain electronic properties of the solid related to the electron-level density at the Fermi surface. Thus in the region of incomplete filling of the *d* band (<60 at.% gold) the catalytic reaction rates are affected through the activation entropy term rather than the activation energy.

The supported Pd–Au catalysts show a somewhat different activity pattern (Fig. 1) whereas the addition of gold at less than 25 at.% leads to an increase in hydrogenation rate; further increases in IB-metal lead to a marked decline in catalytic activity. Since, on the basis of the microsphere results, one would expect further growth in activity up to about 50 at.% gold, we are led to conclude that the surface

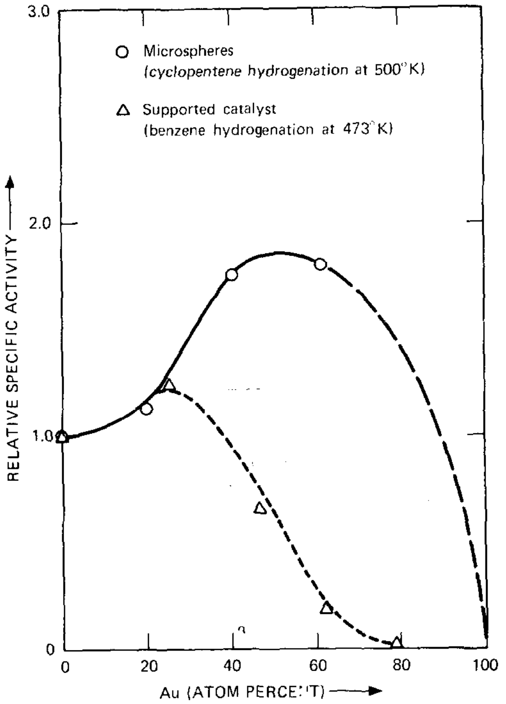

FIG. 1. Activity of Pd–Au catalysts for olefin hydrogenation.

compositions of the crystallites formed on the alumina support are not representative of the bulk alloy composition expected, or recorded by X-ray diffraction. Rather the reacting system encounters a surface phase which is enriched in gold, a situation reminiscent of the Ni–Cu catalysts (*7–9*). These catalytic results are also reflected in earlier measurements of hydrogen chemisorption and surface migration on the same supported alloys (*17*). It is apparent therefore that a miscibility gap is not a requirement for lack of composition equilibrium between the bulk and the surface phases of a mixed-metal catalyst. Differences in surface free energies of the two components of the alloy system combined with differences in the diffusion coefficients will have an important effect on the rate of stabilization of the surface-phase composition, especially in the case of small crystallites. Furthermore, the surface reaction itself may introduce solid-phase concentration gradients which will alter the diffusion rate in excess of that encountered under nonreaction conditions. Such an effect has been suggested in the work on ethylene oxidation over Pd–Ag alloy films (*18*) and the CO sorption on Pt–Au alloy films (*9*).

The question may be raised whether the observed variations in hydrogenation rate as a function of alloy composition for the two types of catalysts may be due to differences in the reactivities of cyclopentene and benzene. Since a cycloolefin may be considered as the intermediate in benzene hydrogenation it is unlikely that the reactivity pattern observed as examined in Tables 3 and 4 is inherent to the reactants used. Rather it reflects the solid-state surface properties of the catalysts employed.

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