The Combination of Hydrogen and Oxygen with on Palladium-Silver Alloys*

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Synopsis

Kinetic measurements of the combination of hydrogen and oxygen on palladium, silver, and their alloys have been made in the temperature range of 80°C and 450°C. Ribbon form samples were used. The change in pressure was measured at a constant volume by an automatic controlling system. It was found that the pretreatment by oxygen raises the reaction rate for palladium, but the effect is not considerable for silver. The apparent activation energy of the reaction remains constant and begins to increase at 60 at % silver with increasing silver content. The activity of a series of alloys rises to a small maximum at about 30 at % silver content. The results are discussed.

I. Introduction

The union of hydrogen and oxygen on the metal surfaces is the one of the typical heterogeneous reactions, but few studies have been reported on this reaction on alloy catalysts. It has been shown that the rate of reaction is of an order between zero and the first with respect to hydrogen and zero or negative with respect to oxygen⁽¹⁾. The results obtained are not unique, even under controlled conditions. The activities of metals are generally variable.

The mechanism of catalytic reaction of the combination of hydrogen and oxygen by palladium is mainly one of alternate oxidation of the metal and reduction of its oxide⁽²⁾. Silver is well known to be an active oxidation catalyst while palladium is not. On the other hand, palladium is a good reduction catalyst and silver is not. These metals are mixible in the whole range and the lattice parameter increases almost linearly from 3.884 Å for palladium to 4.077 Å for silver.

The object of this work is to obtain informations on the alloy catalysts of a heterogeneous reaction. In order to find the role of the band structure of the alloys on the combination reaction, a series of palladium-silver alloys was chosen as catalyst.

II. Experimental

Palladium, silver, and their alloys used were in the form of ribbons, 500 mm long, 2.0 mm wide, and 0.11 mm thickness. The catalysts were annealed at 800°C for 2 hours in vacuo and introduced in the reaction vessel of the capacity of 17.2 mL. The system was evacuated and the catalyst in the vessel was heated at 400°C for 1 minute in hydrogen of a few cm Hg followed by pumping out of the hydrogen for more than 1 hour at the same temperature. The vessel was then cooled down to a desired temperature, the gas mixture of hydrogen and oxygen (2:1) was introduced, and the reaction took place. The same treatments were carried out just before every run. The results obtained are reproducible by these treatments.

The pressure decreases as the reaction takes place. The change in pressure in the system was measured at a constant volume by an automatic controlling system⁽³⁾.

The hydrogen used was prepared by electrolysis of 0.2 N sodium hydroxide. The gas was kept in a reservoir after passing a Pd-asbestos, calcium chloride, phosphorous pentoxide, and solid carbon dioxide-alcohol trap.

Oxygen was also obtained from the anode in the same electrolysis, and was purified by passing through a solid carbon dioxide-alcohol trap followed by activated charcoal

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(1) P.H. Emmett: *Catalysis*, Vol. 1, Reinhold Pub. Co. (1954), 160.

(2) D.J. Chapman, G. Gregory: *Proc. Roy. Soc. A*, **147**(1934), 68.

(3) M. Kowaka: *J. Japan Inst. Metals*, **23**(1959), 655.

cooled at -78°C .

III. Results

The gas mixture of hydrogen and oxygen (2:1) of about 16 cm Hg was admitted into the reaction vessel in which the palladium catalyst was introduced. The change in total

Fig.1 Union of hydrogen and oxygen on palladium. Variation of total pressure with time of reaction in minutes at 100° .

a: Clean palladium.
b: Palladium pretreated by hydrogen.
c: Palladium pretreated by oxygen

no induction period, the reaction takes place rapidly at the start and is completed.

Fig.2 shows the combination of hydrogen and oxygen over silver at 400° . Curves *a*, *b*, and *c* have the same meanings as above. The pressure decreases almost linearly with time differing from a pure palladium.

One of a series of experiments on the Pd-Ag alloys is shown in **Fig.3**. This is the combination of hydrogen and oxygen over 30 at % Ag-Pd alloy at 80° , 100° , and 130° . The reaction takes place after a short induction period. The decrease in pressure against time is almost linear.

When the rate of decrease in pressure against temperature was measured, the apparent activation energy of the reaction can be obtained by the Arrhenius equation, i.e.

$$k = B \exp(-E/RT),$$

Fig.2 Union of hydrogen and oxygen on silver. Variation of total pressure with time of reaction in minutes at 400° .

a: Clean silver.
b: Silver pretreated by hydrogen.
c: Silver pretreated by oxygen.

Fig.3 Union of hydrogen and oxygen on 30 at % Ag-Pd alloy at 80° , 100° and 130° . Variation of total pressure with time in minutes.

where k the rate constant, E the apparent activation energy, R the gas constant, B the constant independent of temperature, and T the absolute temperature.

The rate constants for a series of the alloys are plotted against the reciprocal of absolute temperatures in **Fig.4**. From **Fig.4**, the apparent activation energy as a function of alloy compositions is shown in **Fig.5** (full line). The activation energy remains constant

and begins to rise at 60 at % Ag-Pd alloy. This is the critical composition of the alloys. The activation energy for pure palladium was not obtained because of the complexity of

Fig.4 Variation of rate constant for a series of Ag-Pd alloys with reciprocal of absolute temperature.

Fig.5 Activation energy for the union of hydrogen and oxygen for a series of Ag-Pd alloys. Dashed line denotes the paramagnetic susceptibility after Hoare et al⁽⁴⁾.

the behavior. The paramagnetic susceptibility is shown in the same figure(dashed line)⁽⁴⁾. The susceptibility decreases continuously with increasing silver content until at 60 at % where the holes in the *d*-band in palladium are filled by silver.

Fig.6 shows the variation of activity with composition of the alloys at 100°. The rate of reaction, dp/dt , is plotted against silver content. The activity rises to a small maximum at about 30 at % Ag-Pd alloy. It decreases continuously after that composition and reduces to zero at 70 at % Ag-Pd alloy. If we choose the activities at higher temperatures, this curve may shift upward. The surface areas of the alloys were not measured. They were assumed to be the same. The apparent surface area was 21 cm².

IV. Discussion

The union of hydrogen and oxygen on palladium, silver and their alloys have been studied. Let us consider on pure metals first. For palladium it has an induction period at the start, but no induction period appeared for the catalyst pretreated by oxygen. For

silver, the pressure of gases decreases almost linearly with time and the effect of oxygen pretreatment is not considerable. It is suggested that the difference in reaction on palladium and on silver may be caused by the different ability of these metals for oxygen and hydro-

Fig.6 Rate constant as a function of composition of silver at 100°.

Table 1 Heats of formation of bulk and surface oxides for palladium and silver(kcal/mol) after Bortner & Parravano⁽⁵⁾.

	bulk (298°K)	surface(500°K)
PdO	-21.9	-24.6
AgO	-7.3	-54.0

gen. There is a considerable difference in heats of chemisorption of oxygen on palladium and on silver. The heats of formation of bulk and surface oxides for these two metals

(4) F.E.Hoare, J.C.Matthews, J.C.Walling: Proc. Roy. Soc. A, **216**(1953),502.

are listed in **Table 1**⁽⁵⁾. In the case of bulk Pd-O is more stable than Ag-O, but the surface Ag-O is more stable than the surface Pd-O. Chemisorbed oxygen on palladium can be removed easily by hydrogen but oxygen on silver is not.

As shown in Fig.5, the paramagnetic susceptibility of the alloys decreases continuously and reduces to zero at 60 at % Ag-Pd alloy, while the activation energy for the reaction remains constant until the same composition of the alloys and begins to increase with increasing silver content. It was found that no parallelism can be found between the surface and the bulk properties, except that the abrupt change occurred at the critical composition of the alloys (60 at % Ag-Pd). This composition of alloy is what the holes in the *d*-band are filled by silver. This shows that the sorption of hydrogen plays an important role on the reaction over the alloy catalysts. Because it is generally believed that oxygen chemisorption on metals does not involve direct participation of *d*-electrons.

Finally, the curve of a change in activity of a series of alloys has a maximum at the concentration of 30 at % Ag-Pd alloy. The catalytic activities do not vary continuously with composition of silver as would be expected from the band theory of metals. The activities should decrease continuously with increasing silver content. The cause of the anomalous behavior at 30 at % silver is not clear but may be interpreted by taking consideration of the variation of frequency factor, *B*, in the Arrhenius equation by alloying with silver. Many physical properties rise to a maximum (or minimum) at this composition*. Such a behavior has recently been found on the hydrogenation of benzene over Ni-Cu alloys⁽⁶⁾, but there is no slender explanation. Further studies are needed in order to make sure the above discussion.

V. Conclusions

The following informations on the combination of hydrogen and oxygen over palladium-silver alloys are obtained:

- (1) For pure palladium, there is an induction period at the start followed by a rapid decrease in pressure.
- (2) For silver, the decrease in pressure is a linear function of time and the effect of the pretreatment is not considerable.
- (3) The activation energy of the reaction remains constant and begins to rise at 60 at % Ag-Pd alloy.
- (4) The small maximum activity is found at about 30 at % Ag-Pd alloy.

(5) M.H.Bortner, G.Parravano: *Adv. in Catalysis*, **IX**(1957), 424.

(6) W.K.Hall, P.H.Emmett: *J.Phys. Chem.*, **62**(1958), 817.

* Maximum electric resistivity, mechanical hardness, solubility of hydrogen, and minimum coefficient of thermal expansion.