Oxidation of Carbon Monoxide on Silver Surface

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Introduction

Kinetic studies on a catalytic reaction with the same catalyst have often shown different results by different investigators. On the oxidation of carbon monoxide with silver as catalyst, Benton and Bell[1] showed that the reaction rate was proportional to the pressure of carbon monoxide and independent of the oxygen pressure. On the other hand, Titani et al.[2] showed that the reaction rate was proportional to the oxygen pressure and independent of the carbon monoxide pressure. In both cases the reaction rate was measured by the flow method. The catalyst used by Benton and Bell was the reduced silver catalyst, silver powder prepared by reduction of silver oxide with hydrogen, and those used by Titani et al. were the reduced silver powder and electrolysed silver powder obtained by the electrolysis of acidic silver nitrate solution. The temperature range of experiment was 80–140°C with Benton and Bell, and 150–450°C with Titani et al. Thus the results so obtained by these investigators were inconsistent with each other.

The main aim of the following experiments have been to determine which was the real case, and to make clear why those conflicting results were obtained by the investigators.

Experimental

The measurements of the reaction rate were made by the flow method. The apparatus and procedure employed were almost the same as those used by Titani et al.[2]

Carbon monoxide was generated by dropping formic acid on hot concentrated sulfuric acid. Oxygen was obtained electrolytically from sodium hydroxide solution. Each gas was purified in the usual manner, and stored over water in each reservoir. They were forced out of each reservoir under pressure, dried in the liquid oxygn traps, their flow rate controlled by the glass capillary tubes and inserted wires, and mixed before the entrance of the reaction tube. The total flow rate was fixed at 20 cc. (0°C, 760 mm. Hg.) per min. Controlling the flow rate of each gas, mixed gas having various proportion of carbon monoxide and oxygen were passed over the catalyst at atmospheric pressure. The reaction tube of hard glass was 16 mm. in inside diameter and 230 mm. in length. In the middle of the tube 4 g. of the catalyst was packed ca. 20 mm. in length. The reaction tube was heated by a cylindrical electric furnace.

Both catalysts, the reduced silver powder prepared by reduction of precipitated silver oxide with hydrogen at a low temperature as Benton and Bell[1], and the electrolysed silver powder obtained by electrolysis of acidic silver nitrate solution as Titani et al.[2], were used and compared with each other.

Results

(a) The Experiments with the Reduced Silver Catalyst.

The results are shown in Fig. 1, where the amount of carbon dioxide produced for a minute,

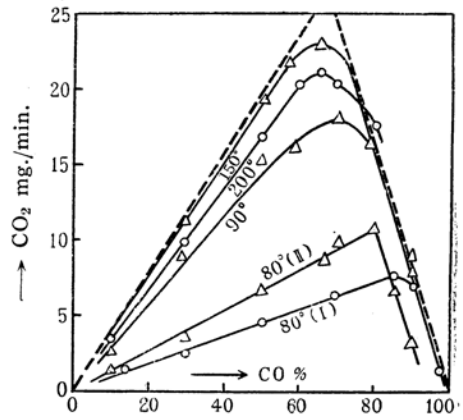

Fig. 1. Reaction rate with reduced silver catalyst.

the reaction rate, is plotted against mole percent of carbon monoxide in the mixed gas. The experiments were made at 80°, 200°, 150°, 90°, and again at 80°C. Benton and Bell[1] made their experiment in two limited composition ranges of the mixed gas, 0–20% and 90–100% of carbon monoxide. Now the reaction rate has been measured in the whole range of carbon monoxide-oxygen composition. The broken line in Fig. 1 shows the boundary, the maximum amount of carbon dioxide allowed for the composition of the mixed gas. Every curve in Fig. 1 increases with carbon monoxide content and falls at the boundary line. Comparing the curves 80° (I) and 80° (II), it is recognized that the catalyst has gradually increased its activity during the experiments. This may be due to the preliminary reduction with hydrogen before every run in order to avoid the deactivation of the catalyst by oxidation during the experiment. The data of the left hand part of every curve, which increases with carbon monoxide content in the

1) A.F. Benton and R.P. Bell, *J. Am. Chem. Soc.*, **56**. 501 (1934).

2) T. Titani and T. Ishiwatari, *J. Am. Chem. Soc.*, **65**, 13 (1944); T. Titani and N. Yamada, *ibid*, **65**, 224 (1944); T. Titani and S. Nakata, *ibid*, **65**, 305 (1944).

mixed gas, obey the following relation.

$$v = kP_{CO} \qquad (1)$$

where v is the reaction rate, number of mg. of carbon dioxide produced in one minute, k is the rate constant, and P_{CO} is the average partial pressure of carbon monoxide in the entering and exit mixed gas. Though the reaction rate in these experiment was larger than those of Benton and Bell[1], the kinetic relation (1) was qalitatively the same as theirs. That is, the reaction rate is proportional to the pressure of carbon monoxide and independent of the oxygen pressure.

(b) The Experiments with the Electrolysed Catalyst.

In the first experiment the electrolysed catalyst well-washed and dried was used without preliminary reduction with hydrogen. The results at

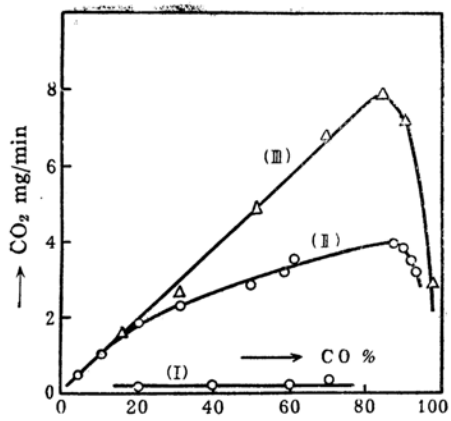

Fig. 2. Reaction rate with electrolysed silver catalyst at 80°C.

80°C are plotted as (I) in Fig. 2. The amount of carbon dioxide produced was very small. Then the catalyst was reduced in the hydrogen stream at 200°C for thirty minutes. The results of the second experiment after this treatment are plotted as (II) in Fig. 2. The catalyst was markedly activated and the reaction rate increased with the partial pressure of carbon monoxide. The data of the experiment with the reduced silver catalyst at 80°C, 80°(1) in Fig. 1, are plotted in Fig. 2 as (III) for comparison. It can be seen that by reduction with hydrogen the electrolysed catalyst was activated and approached to the reduced silver catalyst prepared from silver oxide.

(c) The Effect of Reduction and Poisoning with Hydrogen.

As mentioned above, it may be thought that when the surface of the silver catalyst has been fully reduced, the reaction rate increases with the partial pressure of carbon monoxide, the '*ascending*' type like the curve (II) and (III) in Fig. 2. If so, the surface of silver catalyst, which showed such low activity as (I) in Fig. 2 might have been oxidized or poisoned with oxygen. To make sure of this, the following experiment was made. The results are shown in Fig. 3. The electrolysed silver catalyst dried but not reduced preliminarily with hydrogen was used. The reaction rate was measured at 200°C in the first, the curve (I) in Fig. 3. The reaction rate decreased with carbon monoxide content in the mixed gas. The curve (I) in Fig. 3 is the '*descending*' type. This is the same type of curve as has been seen

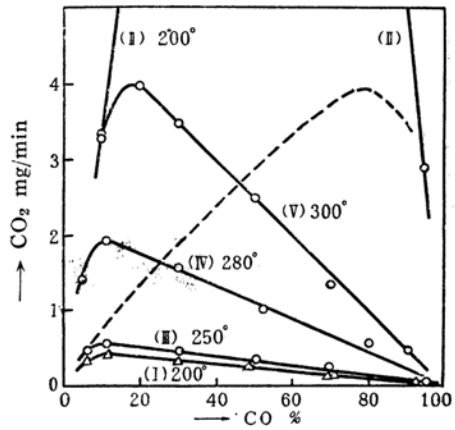

Fig. 3. Reaction rate with electrolysed silver catalyst and its changes by reduction and oxygenation.

in the experiment of Titani *et al*[2]. After the reduction of this catalyst in the hydrogen stream at 200°C, the reaction rate was measured again at 200°C. As was expected, the catalyst was remarkably activated, and the mixed gas reacted almost completely during the passage of the catalyt layer as was seen partially by (II) in Fig. 3. Then the catalyst was heated at 300°C in an oxygen stream for four hours, in order to poison the silver surface with oxygen. The results of three series of experiments at 250°, 280° and 300°C after this treatment are shown as (III), (IV), and (V) in Fig. 3. Clearly the catalyst was deactivated and the curves were of the '*descending*' type. The data on the straight line parts of these curves obey the following relation.

$$v = k'P_{O_2} \qquad (2)$$

where v is the reaction rate as the equation (1), k' is rate constant, and P_{O_2} is the average partial pressure of oxygen in the mixed gas. The reaction rate was proportional to the partial pressure of oxygen and independent of the carbon monoxide pressure. This was the case in the experiment of Titani *et al.*[2] For comparison with the curve (II) in Fig. 2, the results of the experiment at 80°C on the electrolysed silver catalyst reduced with hydrogen, is drawn into Fig. 3 as the broken line curve. It can be seen that the type of the curves is changed from '*ascending*' into '*descending*' type. The experiments by the use of the reduced silver catalyst from silver oxide was made also in a procedure similar to the above, and the same change by the treatment with oxygen could be seen.

Discussion

The results of the above experiments are

summarized and represented schematically in Fig. 4.

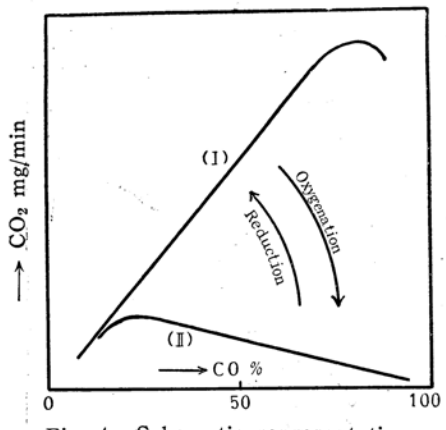

Fig. 4. Schematic representation of results.

When the surface of the silver powder has been fullly reduced with hydrogen, the rate of the catalytic oxidation of carbon monoxide on the surface describes the '*ascending*' type of reaction rate-composition curve as shown in Fig. 4 (I). The rate of reaction increases proportionally to the partial pressure of carbon monoxide and independently to the oxygen pressure. This is the case when the silver powder has been prepared by electrolysis of silver nitrate solution as well as by reduction of silver oxide. On the other hand, when the surface of silver powder has not been fully reduced or poisoned with oxygen, the catalyst is less active, and the reaction rate-composition curve is the '*descending*' type like (II) in Fig. 4. The reaction rate increases with the partial pressure of oxygen and is independent of the carbon monoxide pressure. This is the case when the catalyst is of the reduced silver from silver oxide as well as of the electrolysed silver. The 'ascending' type (I) in Fig. 4 corresponds to the result of the experiment of Benton and Bell[1], and the 'descending' type (II) corresponds to that of Titani et al[2]. One of these two different features of reaction rate dependency can be changed to the other by heating the surface of the silver catalyst in the stream of oxygen, or hydrogen.

These results indicate the following mechanism of oxidation of carbon monoxide on silver surface. This catalytic reaction consists mainly of the following two steps.

(i) $O_2 \longrightarrow 2O$ (chemisorption)

(ii) $O + CO \longrightarrow CO_2$

The step (i) is the chemisorption of oxygen on the surface of the silver catalyst. The oxygen molecules in the gas phase collide against the bare catalyst surface and are chemisorbed into atoms on it. In the next step (ii) the carbon monoxide molecules in the gas phase strike the chemisorbed oxygen on the surface of the silver catalyst and combine with them into carbon dioxide. If this is the mechanism of oxidation of carbon monoxide with silver catalyst, the following two limiting cases may occur.

(I) The case in which plenty of oxygen is chemisorbed on the catalyst surface.

In this case the amount of chemisorbed oxygen on a unit area of the surface of the silver catalyst must be large enough, and almost independent of the oxygen pressure. In consequence the reaction rate may be proportional to the rate of collision of carbon monoxide molecules on the catalyst surface, and accordingly to the partial pressure of carbon monoxide. That is,

$$v = kP_{CO}$$

This is the case when the silver powder prepared by the reduction of silver oxide with hydrogen is used, or generally when a silver catalyst has been treated with hydrogen and the catalyst surface has been fully reduced.

The activation energy for this case was calculated by the relation of the rate constant and the reaction temperature of the experiment (a) with the reduced silver catalyst.

$$A = 4.9 \text{ kcal.}$$

It may be presumed that the activation energy has the following content.

$$A = A_2 - Q/2$$

A_2 is the activation energy of the reaction step (ii), and Q is the heat of reaction step (i), or the heat of chemisorption of oxygen on the catalyst surface.

(II) The case in which only a little oxygen is chemisorbed on the catalyst surface.

In this case oxygen, as soon as it is chemisorbed on the catalyst surface, combines instantly with carbon monoxide. In consequence the total reaction rate is determined by the rate of chemisorption of oxygen on the catalyst surface. Accordingly it is proportional to the partial pressure of oxygen and independent of the carbon monoxide pressure, as following

$$v = k'P_{O_2}$$

This is the case when the electrolysed silver catalyst not reduced is used, or generally when a silver catalyst has been treated with oxygen and poisoned the surface.

The activation energy was calculated from the data of the experiments (III), (IV), and (V) in Fig. 3.

$$A' = 23.6 \text{ kcal.}$$

This activation energy A' must be the activation energy A_1 of the reaction step (i), or of chemisorption of oxygen on this poisoned catalyst surface.

$$A' = A_1$$

Thus, it can be explained by the above consideration that the different features of the reaction appear with reduction or oxydation of a catalyst surface. It my be concluded that Benton and Bell measured the reaction rate on the fully reduced silver surface, and that Titani et al. on the surface poisoned with oxygen. The difference between the two is by no means contradictory.

Summary

The catalytic oxidation of carbon monoxide on the surface of silver powder has been studied. The reaction rate has been measured by the flow method. The reaction rate on the fully reduced silver surface is proportional to the pressure of carbon monoxide and independent of the oxygen pressure. On the other hand, when the surface has not been reduced with hydrogen, or has been treated preliminarily in an oxygen stream at a high temperature, the reaction rate is proportional to the oxygen pressure and independent of the carbon monoxide pressure. One of these two features of the reaction can be changed to the other by heating the surface in the stream of oxygen, or hydrogen. These results indicate that the chemisorption of oxygen and the reaction between this chemisorbed oxygen and carbon monoxide are the main steps of the oxidation, and its reaction rate is determined by either of these steps.

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