An Anomalous Catalytic Activity of Reduced Silver

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Introduction

Though metallic silver is often used an oxidation catalyst, its activity does not seem clarified yet in spite of its simple structure as compared to that of defect catalysts. In the course of our study[1,2] on the isotopic exchange reaction between heavy oxygen and carbon dioxide, $O^*_{ads.} + CO_2 \rightleftarrows O_{ads.} + COO^*$, we were obliged to conclude that even when the silver catalyst is reduced at 300°C for five hours before each run, there remain some chemical species containing oxygen which can exchange with the gaseous one. As the experiment was carried out under the partial pressure of oxygen of about 70 mmHg, the formation of silver oxide is improbable from the view point of thermodynamics[3]. On the other hand, as the exchangeable oxygen was found to exist in so great an amount that it is of comparable order of magnitude to that which was monomolecularly adsorbed[4], it was presumed that they may remain as an occluded state in the layers very close to the surface (subsurface) rather than as the adsorbed state on the surface. Both sorts of oxygen-containing species may probably be oxygen atoms, as assumed in the present paper and also by other researchers[5,6] in which, however, only the adsorbed state was considered.

The present research was begun in order to support the above presumption with experimental facts, studying the behaviour of oxygen adsorbed by the silver catalyst in detail, with special regard to the method of reduction of the catalyst. To meet the object, the exchange reaction between adsorbed oxygen and carbon dioxide was utilized as well as the reaction between adsorbed oxygen and carbon monoxide, $O_{ads.} + CO \longrightarrow CO_2$, which can easily occur even at room temperature[5].

Experimental

The catalyst (10.0 g.) was newly prepared by reducing the silver oxide with a flow of hydrogen gas at 300°C, similarly as in the previous reports[1,2]. Preparation of the silver oxide was different only in the procedure that, instead of ammonium hydroxide, it was precipitated by barium hydroxide as done Benton et al.[7]. The precipitated silver oxide was washed with distilled water free from carbon dioxide, until no barium ion was detected in the filtrate. It was found that this catalyst has a normal lattice distance 4.086 Å, as compared to the values in the tables*. The catalyst was reduced again in each run before the experiments at 250°C or 275°C to minimize the possible sintering of the catalyst.

The apparatus is shown in Fig. 1, its wall was made of hard glass, the reaction tube was 119 ±1 cc. (NTP) and the catalyst was spread on the wall of the tube a few millimeters in thickness. The temperature of the furnace was kept constant within ±1°C for a few hours and within ±5°C for a few days by the use of an automatic controlling device.

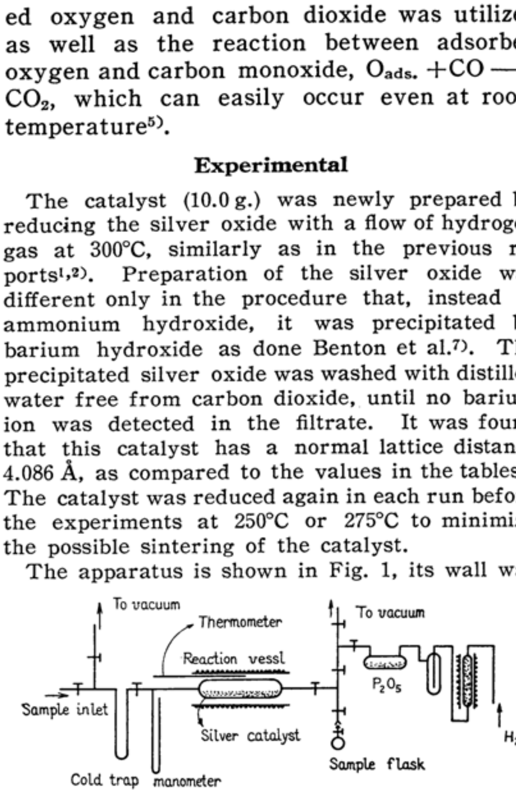

Fig. 1. Schematic diagram of the apparatus

The heavy oxygen (OO*) used was prepared in our laboratory by a thermal diffusion column, its molar isotopic concentration being 2.58%. The abundance ratios of OO^*/O_2 and COO^*/CO_2 were determined mass-spectrometrically. The accuracy of one determination of the abundance ratio was ±0.05%.

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[1] H. Mori, K. Hirota and Y. Kobayashi, This Bulletin, **28**, 532 (1955).

[2] H. Mori, Y. Kobayashi and K. Hirota, *Shokubai*, **12**, 34 (1955).

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

[4] Y. Kobayashi, K. Hirota and T. Otaki, unpublished.

[5] D. Garvin, *J. Am. Chem. Soc.*, **76**, 1581 (1954).

[6] cf. T. Titani et al., *J. Chem. Soc. Japan*, **55**, 13, 224, 305 (1934).

[7] A. F. Benton and L. C. Drake, *J. Am. Chem. Soc.*, **54**, 2186 (1932); **56**, 255 (1934).

* Landolt-Börnstein, 6. Aufl., 4.077$_8$ KX (25°C); Natl. Bur. St., 4.086$_2$ Å.

TABLE I

EXPERIMENTAL RESULTS (Reaction Temperature: 200°C)

No. of Runs	Time of the 1st Outgassing (hr.)	Press. before the Reduction (mmHg)	Reduction Time (hr.)	Time of the 2nd Outgassing (hr.)	Initial Gas and Press. (mmHg)	OO*, CO* or COO* % in the Gas	OO* or COO* % in Gas after the Reaction (Time in hr.)		
I.	Experiment I			(Reduction Temperature 250°C)					
1	—	$\sim 10^{-6}$	8	4	O_2 76	2.58	2.36 (1/3)	2.08 (1)	1.82 (25)
2	3	2×10^{-4}	10	5	O_2 82	2.58	2.58 (0.5)	2.44 (16.5)	
3	5.5	1×10^{-4}	18	4	CO_2 24	0.40	0.92 (3)	—	
4	3.5	5×10^{-5}	40(7)	4	O_2 73	2.58	—	2.41 (18)	
II.	Experiment II			(Reduction Temperature: 275°C)					
5	5.5	1×10^{-5}	65(16)	6	O_2 61	2.58	2.58 (3)	2.46 (18)	
6	4	3×10^{-5}	—	—	CO_2 29	0.40	0.87 (3)	0.98 (20)	
7	24	$\sim 10^{-4}$	18(3)	4	O_2 91	2.58	2.58 (3)	2.48 (44)	
8	5	$\sim 10^{-5}$	18(3)	5	CO_2 70	0.40	0.46 (3)	0.43 (19)	
9	4	$\sim 10^{-5}$	18.5(3)	5.5	CO 58	0.20	0.20 (3)	0.20 (20)	
10	5	$\sim 10^{-5}$	18(3)	5	O_2 50	0.40	0.68 (3)	0.92 (20)	

N. B.

Pressure of the second outgassing need not be described, because it reached to 10^{-6} mmHg within a few minutes. The first outgassing of No. 5 was carried out at 250°C. Numerals in parentheses in the fourth column designate the time of reduction by flowing hydrogen gas.

Results

All the experiment which is shown in Table I was performed, in the order of the number of runs, and can be divided into I and II.

The first experiment (I) was done, in order to confirm the conclusion reported already that some chemical species containing oxygen atoms remain in the catalyst even after the reduction by hydrogen. Hereafter this sort of oxygen will be called the residual oxygen, the existence of which was really shown by the reduction at 250°C, as will be described.

By the decrease of concentration of heavy oxygen in the gas (No. 1) eight hours' contact of hydrogen was insufficient to remove all the residual oxygen, while by the repeated treatment of heavy oxygen these kinds of oxygen were fairly replaced by the heavy ones (No. 2). This catalyst was then treated by normal carbon dioxide in the next run (No. 3), by which the possible exchange effect with heavy oxygen charged in the catalyst was observed. The dilution of the heavy oxygen which ought to be brought about by this procedure was confirmed by the next run (No. 4). In this run, notwithstanding the fact that the catalyst was reduced for forty hours, for seven of which hydrogen gas was allowed to flow over the catalyst the decrease of heavy oxygen concentration was observed to the degree equivalent to the dilution which occurred in No. 3. It seems that because of the process of severer reduction, the object, to charge the catalyst with heavy oxygen, was practically attained by only one run.

As the existence of oxygen in the catalyst even after the reduction at 250°C was shown by the above experiment, the second experiment (II) was carried out, in order to investigate its nature in detial, i. e., presumption in the former report. In the present series of runs, the reduction and degassing temperatures were raised from 250°C to 275°C, so as to remove the oxygen occluded as much as possible.

In the run next to No. 4, heavy oxygen was again diluted (No. 5), when it was brought into contact with the catalyst, probably because of a severer condition than in Exp. I. Then if the catalyst was only degassed and not reduced before the introduction of carbon dioxide, the exchange effect was observed as in No. 3, suggesting that exchangeable oxygen remains on the surface (No. 6). However, if the catalyst was reduced (No. 7) and was again brought into contact with carbon dioxide (No. 8), it seemed that the above oxygen had been removed, because in this run, the isotopic composition of the carbon dioxide did not change practically. Moreover, it was found in No. 9 that carbon monoxide neither exchanges nor reacts with the residual oxygen as shown by the constancy of its isotopic composition and its pressure. However, the possible suspicion that heavy oxygen might already be removed completely was rejected by making normal oxygen contact with the catalyst (No. 10); i. e., heavy oxygen still remained in the catalyst after the repeated reduction process before the commencement of three runs (No. 8, 9 and 10).

Discussion

Now, the above result will be discussed in more details. First, if it is assumed that the concentration of the residual oxygen in the catalyst is 2.48% (No. 7) and that an equilibrium is realized between normal oxygen and the residual heavy oxygen after twenty hours of contact (No. 10), giving 0.92% as the concentration of the latter, the total amount of oxygen per gram-catalyst remaining in the catalyst, if expressed by gaseous volume (NTP), will be given by

$$69\,\text{cc.}\times\frac{0.92-0.40}{2.48-0.92}\times\frac{50(\text{cm.})}{760(\text{cm.})\times 10.0\,\text{g.}} = 0.15_1\ \text{cc./g.-cat.} \qquad \text{(A)}$$

considering that the gaseous volume in the tube at 200°C corresponds to 69 cc. (=119 ×273/473) at NTP, and neglecting the effect of isotopic separation.

According to our adsorption measurement[4], the amount of oxygen monomolecularly adsorbed on the surface is 0.069 cc./g.-catalyst at 200°C, so the numeral obtained in (A) is twice as large as the present one. Second, by the similar reasoning as the above, the volume (NTP) of oxygen remaining after the evacuation will be estimated by the data of No. 6 and 7 as follows:

$$69\,\text{cc.}\times\frac{0.98-0.40}{2.48-0.98}\times\frac{29(\text{cm.})}{760(\text{cm.})\times 10.0\,\text{g.}} = 0.10_2\ \text{cc./g.-cat.} \qquad \text{(B)}$$

It is found that the amount of exchangeable oxygen is smaller in this case but larger than that absorbed on the surface, suggesting that most of the exchange reaction seems to proceed between the normally adsorbed oxygen and carbon dioxide.

Thus it is made clear that metallic silver, though easily reducible, retains oxygen atoms firmly even when the reduction was performed carefully. Though the existence of non-removable oxygen was already reported by Benton and Bell[3], it can be shown by the present investigation that such oxygen in the catalyst is not restricted to one kind of state. It may exist as an adsorbed state on the surface, but also as a state more firmly bound, e.g., in the subsurface rather than to the adsorption to a special part of the surface. Because, by the curious behavior shown in No. 8, 9 and 10, most firmly bound oxygen (" residual oxygen ") can neither exchange with carbon dioxide nor react with carbon monoxide, but, contrary to our expectation, it can exchange with gaseous oxygen.

The above behaviour can be explained analogously by the scheme proposed by Garner et al.[8], in the case when cuprous oxide is in contact with oxygen; i.e., when oxygen is brought into contact with the silver surface, silver atoms on the surface will migrate so as to cover some of the oxygen atoms, and the oxygen atoms thus covered will exchange with the residual oxygen atoms. On the other hand, as both carbon dioxide and carbon monoxide are slightly adsorbed to silver, probably to such a degree as one-hundredth of oxygen[4] even if they are adsorbed such migration cannot occur in case of contact with these gases. It is natural, therefore, that the exchange reaction was not observed in No. 8 and 9. However, the process of migration will not continue infinitely into the silver bulk-phase, as can be expected for the thermodynamical reason. This is actually realized by the fact that the amount of adsorbed oxygen remains to the degree, corresponding to one or two layers. However, as the isotopic effect in adsorption equilibrium is not taken into consideration the quantitative discussion on this matter will not be developed further.

Conclusion

From the different catalytic behaviour of reduced silver against carbon dioxide, carbon monoxide and oxygen, it may be concluded that the silver retains a special kind of " residual oxygen " firmly after it is brought into contact with oxygen, even at above the temperature region, at which the dissociation of silver oxide would begin.

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[8] W. F. Garner, F. S. Stone and P. F. Tiley, *Proc. Roy. Soc.*, **A211**, 472 (1952).