Correlation between Thermodynamic Quantities of Adsorbed Oxygen and Selectivity for Ethylene-Oxide Formation on Silver

Masahiro SEO* and Norio SATO*

Oxygen adsorption on three catalysts of pure silver having different activities was measured in the temperature range 200°C–270°C by using a high sensitivity micro-balance, and the thermodynamic quantities such as differential free energy of adsorption $\Delta G_{ads}$, differential heat of adsorption $\Delta H_{ads}$ and entropy of adsorbed oxygen $S_{ads}$ at 230°C in case of the oxygen coverage, $\theta$, of 0.7 were estimated.

Comparison was made of the selectivity for ethylene oxide at 250°C with the thermodynamic properties estimated at 230°C in case of $\theta = 0.7$, and it was found that the selectivity for ethylene oxide increases as $\Delta H_{ads}$ decreases and $S_{ads}$ increases. Theoretical calculation of the entropy of adsorbed oxygen was also made with the result that the adsorbed molecular oxygen, $O_2\text{ad}$ has the larger entropy than the adsorbed atomic oxygen, $O\text{ad}$.

Therefore it is likely that the selectivity for ethylene oxide formation is attributed mainly to the adsorbed molecular oxygen, $O_2\text{ad}$.

1 Introduction

The partial oxidation of ethylene to ethylene oxide can take place on silver, while usually ethylene is completely oxidized on metals other than silver. This may be attributed to the binding state of adsorbed oxygen on silver the affinity of which to oxygen is positive at ordinary temperatures but negative at high temperatures. In the recent literatures, silver has been suggested to adsorb oxygen on its surface in two different forms, atomic and molecular oxygen; it is molecular oxygen that has frequently been assumed to be responsible for producing ethylene oxide.

In this work, the oxygen adsorption on three catalysts of pure silver having different activities was measured by using a high sensitivity micro-balance, and the thermodynamic quantities such as differential free energy of adsorption $\Delta G_{ads}$, differential heat of adsorption $\Delta H_{ads}$ and differential entropy of adsorption $\Delta S_{ads}$ were estimated. These results were then discussed referring to the catalytic activity for ethylene oxide formation.

2 Experimental

Three different silver catalysts were used. Catalyst A was prepared by reducing commercial grade silver (1) oxide in pure hydrogen gas at 250°C for 4 hours. Catalyst B was prepared by the same method as described by Hirasa and Hirayama. First, an alkaline solution (36.5 g KOH in 300 ml H$_2$O) was carefully dropped into a AgNO$_3$ solution (27.3 g AgNO$_3$ in 300 ml H$_2$O) at 5°C to obtain a mixture of solution and silver (1) oxide precipitate, to which 12.5 ml of 30 per cent HCHO solution was added. This mixture was kept at 5°C for 30 minutes and then boiled for one hour. The precipitate was then filtered, washed with distilled water, treated in 2 percent HNO$_3$ solution for 2~3 minutes and washed again with distilled water until no nitric ions were detected. The precipitate thus obtained was dried at 80°C and reduced to silver powder in pure hydrogen gas at 250°C for 4 hours. Catalyst C was prepared in the same way as that of catalyst B, except for the descent of the temperature from 5°C to −5°C for the precipita- tion and 30 minute aging with HCHO.

A high sensitivity auto-recording thermobalance of closed type (Cahn Co., Ltd.) was used for measuring the weight of adsorbed oxygen: the sensitivity was claimed to be $10^{-7}$ g/div. with the specimen weight of 2 g and the vacuum attainable to be $10^{-5}$ torr. Before measurements, the silver catalyst placed in the balance was heated at 250°C in purified hydrogen gas at 10 torr for one hour to reduce any oxide film and then 10 torr of hydrogen was replaced by 200 torr of pure argon: The argon atmosphere of 200 torr was chosen to reduce the damping of the balance system.
that often encountered when introducing oxygen directly into the evacuated balance. For a series of measurements the same catalyst was used repeatedly with the hydrogen treatment.

The measurement of the catalytic activity for ethylene partial oxidation was carried out at 250°C, using a cylindrical reaction vessel made of glass 1.5 cm in diameter, 15 cm in length with the catalyst 2 g in weight and the reaction gas, 2.8 per cent ethylene, 6.3 per cent oxygen and 90.9 per cent argon, at the flow rate of 64 cc/min. A gas chromatograph of hydrogen flame ionization type was used to analyze the composition of the reaction product.

3 Results and Discussion

3.1 Isotherm of Oxygen Adsorption

Fig. 1 shows the isotherms of oxygen adsorption on three silver catalysts at various temperatures and Fig. 2 is a plot of the reciprocal of the adsorbed oxygen weight against the reciprocal of the oxygen pressure in equilibrium at 230°C. It is seen that the adsorption isotherm fits fairly well to a Langmuir equation of molecular adsorption:

\[ q = \frac{q_m K P_{O_2}}{1 + K P_{O_2}} \]  

(1)

Here, \( q \) is the weight of adsorbed oxygen, \( q_m \) the monolayer weight of molecular oxygen adsorption and \( K \) the equilibrium constant of the adsorption. Equation (1) can be rewritten as

\[ \frac{1}{q} = \frac{1}{q_m} + \frac{1}{q_m K} \cdot \frac{1}{P_{O_2}} \]  

(2)

The constants, \( q_m \) and \( K \), can be estimated from the results shown in Fig. 2, and the estimated values of the constants for the three silver catalysts are shown in Table 1.

\[ \frac{1}{P_{O_2}} \text{ (torr}^{-1}) \]

![Fig. 2 Langmuir isotherm plots of oxygen adsorption at 230°C for three catalysts A, B and C](image)

Table 1 \( q_m \) and \( K \) of three catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( q_m )</th>
<th>( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.5\times10^{-4} g</td>
<td>1.6\times10^6 atm^{-1}</td>
</tr>
<tr>
<td>B</td>
<td>1.1\times10^{-4} g</td>
<td>4.1\times10^6 atm^{-1}</td>
</tr>
<tr>
<td>C</td>
<td>5.3\times10^{-4} g</td>
<td>3.1\times10^6 atm^{-1}</td>
</tr>
</tbody>
</table>

3.2 Calculation of \( \Delta H_{ads} \), \( \Delta G_{ads} \), \( \Delta S_{ads} \) and \( S_{ads} \)

The differential heat of oxygen adsorption, \( \Delta H_{ads} \), can be calculated from the isotherms shown in Fig. 1 by using the Clausius-Clapeyron equation:

\[ H_{ads} = R \left( \frac{d \ln P_{O_2}}{d(1/T)} \right)_\theta \]  

(3)

where \( P_{O_2} \) is the equilibrium oxygen pressure, \( R \) the gas constant and \( \theta \) the coverage of adsorbed oxygen on the surface, which is represented by \( q/q_m \).

In Fig. 3, the logarithm of \( P_{O_2} \) at constant coverage is plotted against the reciprocal of temperature, from which we can estimate \( \Delta H_{ads} \). \( \Delta H_{ads} \) thus estimated is shown as a function of \( \theta \) in Fig. 4. Since calculation of \( \Delta H_{ads} \) at the oxygen coverage below \( \theta = 0.6 \) and above \( \theta = 0.8 \) in Fig. 4 was made from extrapolation of the measured oxygen adsorption isotherms, some inaccuracy can not be avoided. Therefore, only the values of \( \Delta H_{ads} \) in case of \( \theta = 0.7 \) will be discussed here. In case of \( \theta = 0.7 \), \( \Delta H_{ads} \) is seen to be

\[ * \] Actually, \( q_m \) decreases with raising the temperature. For the purpose of comparison, however, we may take \( q_m \) as a constant temperature as the monolayer adsorption to calculate the oxygen coverage of three catalysts. In the above calculation, \( q_m \) at 230°C was used.
Since the entropy of oxygen in the three-dimensional gas standard at 230°C is 52.7 e.u.\(^0\), the entropy of adsorbed oxygen, \(S_{ads}\), is estimated to be \(S_{ads} = (52.7 + dS_{ads})\) e.u.

Table 2 \(dH_{ads}, dG_{ads}, dS_{ads}\) and \(S_{ads}\) at 230°C in case of \(\theta = 0.7\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(dH_{ads}) (kcal/mol)</th>
<th>(dG_{ads}) (kcal/mol)</th>
<th>(dS_{ads}) (cal/mol K)</th>
<th>(S_{ads}) (cal/mol K)</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>-18</td>
<td>-4.4</td>
<td>-27</td>
<td>25.7</td>
</tr>
<tr>
<td>B</td>
<td>-12</td>
<td>-4.7</td>
<td>-14.5</td>
<td>38.2</td>
</tr>
<tr>
<td>C</td>
<td>-16</td>
<td>-4.9</td>
<td>-22.1</td>
<td>30.6</td>
</tr>
</tbody>
</table>

3.3 Catalytic activity

After several measurements of oxygen adsorption isotherm, the catalytic activities of three silver catalysts were measured.

Fig. 5 shows the time-variation of the catalytic activity for the three catalysts, in which X indicates the total conversion of ethylene, Y the partial conversion to CO\(_2\) and H\(_2O\), and Z the partial conversion to C\(_2\)H\(_2\)O\(_2\), and S the selectivity for C\(_2\)H\(_2\)O\(_2\). It is seen that at the reaction time of two hours, the selectivities for ethylene oxide of catalysts A, B and C are 11 per cent, 72 per cent and 35 per cent, respectively; in two hours the surface states of three silver catalysts became stable, and the catalytic activities became constant against time.

3.4 Selectivity relating to thermodynamic quantities of oxygen adsorption

It is evident from comparison of the selectivity for ethylene oxide at 250°C and the thermodynamic properties estimated at 230°C in case of \(\theta = 0.7\) that, as \(dH_{ads}\) decreases and \(S_{ads}\) increases, the selectivity for ethylene oxide increases. This suggests that the adsorbed oxygen in the rate of small \(dH_{ads}\) and large \(S_{ads}\) mainly contributes to the formation of ethylene oxide. A small heat of adsorption means a relatively
weak bond between the adsorbent silver and the adsorbate oxygen, and a large entropy means that the adsorbed oxygen is easily mobile on the surface.

Oxygen isotope exchange studies by Margolis\textsuperscript{13} and our conductivity studies\textsuperscript{19} have shown that the molecular form and atomic form of adsorbed oxygens can be coexist on the surface of silver. Czanderna\textsuperscript{7} in his micro-balance study of oxygen desorption from a silver surface classified adsorbed oxygens into several groups depending on the bond strength between oxygen and silver, and persisted that weakly chemisorbed oxygen is in the form of molecule, $O_2\text{ad}$ and strongly chemisorbed oxygen in the atomic form, $O\text{ad}$. The weak bond between oxygen and silver may correspond to the high mobility of oxygen on the surface. If the adsorbed molecular oxygen, $O_2\text{ad}$ can translate and rotate freely on the two-dimensional surface and if the adsorbed atomic oxygen, $O\text{ad}$ is localized at fixed sites on the surface, the difference between the entropy of adsorbed atomic oxygen, $S_{\text{atom}}$ and the entropy of adsorbed molecular oxygen, $S_{\text{mol}}$ on the surface may be written by:

$$S_{\text{trans}} = R \ln MTa + 65.8 \text{e.u.}$$

where $M$ is the molecular weight of oxygen and $a$, the effective area occupied by a oxygen molecule with 14.1 A$^2$. Hence, we obtain $S_{\text{trans}} = 17.1 \text{e.u.}$ for the adsorbed molecular oxygen at 230\,$^\circ$C. The entropy of rotation of molecular oxygen on the surface is given by Halford\textsuperscript{9} as follows:

$$S_{\text{rot}} = \frac{h^2}{8\pi^2 k} \left[ \frac{1}{\pi a} \left( \frac{\pi T}{\Theta_a} \right)^{1/2} + \frac{1}{4} \right],$$

where $a$ is the symmetry number of the molecule, $h$ the Planck constant and $I$ the moment of inertia. Since $a=2$ and $\Theta_a=2.07$ for oxygen molecule, we obtain at 230\,$^\circ$C $S_{\text{rot}} = 4.0 \text{e.u.}$

The dissociation entropy of oxygen molecule on the surface is given by Chang\textsuperscript{10} as follows:

$$S_D = 2 \left[ \frac{1}{\pi a} \ln \left( \frac{3}{4} \right) \right]$$

where $1/X$ is the surface coverage with oxygen. Equation (8) gives us for the adsorbed oxygen $S_D = 3.7 \text{e.u.}$ in case of $\theta = 0.7$. The difference of the entropy between atomic and molecular oxygens at 230\,$^\circ$C is given by $dS = S_{\text{mol}} - S_{\text{atom}} = 17.4 \text{e.u.}$. This value may be compared with 10.6 e.u. given in literature\textsuperscript{7} for the entropy difference between gaseous molecular oxygen and atomic oxygen.

Since the entropy of adsorbed molecular oxygen, $O_2\text{ad}$ is larger than that of adsorbed atomic oxygen, $O\text{ad}$ the mean entropy of adsorbed oxygen should increase as the ratio of molecular oxygen increases. Therefore, the order in the amount of entropy of adsorbed oxygen for the three catalysts, A, B and C, would correspond to the order in the ratio of adsorbed molecular oxygen, $O_2\text{ad}$ to the total adsorbed oxygen on the surface of these catalysts. As shown in Table 2, the entropy of adsorbed oxygen increases in the order, catalyst A, catalyst C, and catalyst B. On the other hand, it is seen in Fig. 5 that the selectivity for ethylene oxide formation increases in the same order as above.

It is therefore likely that the selectivity for ethylene oxide formation is attributed mainly to the adsorbed molecular oxygen, $O_2\text{ad}$.

4 Conclusion

Oxygen adsorption on three catalysts of pure silver having different activities was investigated from the standpoint of view of thermodynamics.

From the comparison between the selectivity for ethylene oxide formation at 250\,$^\circ$C and the thermodynamic quantities of adsorbed oxygen estimated at 230\,$^\circ$C in case of the oxygen coverage, $\theta$, of 0.7, and from the theoretical calculation of the entropy of adsorbed oxygen, the following conclusions were deduced:

1) The selectivity for ethylene oxide formation increases as the differential heat of oxygen adsorption, $dH_{\text{ads}}$, decreases and the entropy of adsorbed oxygen, $S_{\text{ads}}$, increases.

2) The adsorbed molecular oxygen, $O_2\text{ad}$ has the larger entropy than the adsorbed atomic oxygen, $O\text{ad}$.

3) The adsorbed molecular oxygen, $O_2\text{ad}$ is more contributive to the formation of ethylene oxide than the adsorbed atomic oxygen, $O\text{ad}$.

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References: