Korean J. of Chem. Eng., 6(4) (1989) *300-305*

THE EFFECT OF OXYGEN ON THE CHEMISORPTION ON POLYCRYSTALLINE SILVER SURFACE

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(Received 22 February 1989 • accepted 1 June 1989)

Abstract—The adsorption of oxygen(O_2) and the effect of oxygen on the chemisorption of water(D_2O) and hydrogen(D_2) on polycrystalline silver surface have been studied using the technique of thermal desorption spectroscopy(TDS) under ultra-high vacuum(UHV) condition. Three different states of adsorbed oxygen are observed on the surface. The adsorptions and reactions of water and hydrogen on the oxygen-dosed surface are strongly affected by the pre-adsorbed oxygen. Water on the oxygen-dosed surface shows a maximum desorption at 430K. During the adsorption of hydrogen on the oxygen-dosed surface, hydrogen is rapidly oxidized by a stepwise reaction in which hydrogen reacts first with O(a) to yield hydroxyl intermediate[OD(a)] and then this intermediate reacts to form water. The rate-determining step in this reaction is desorption of water.

INTRODUCTION

Silver is a unique catalyst in some industrial processes, especially the epoxidation of ethylene to ethylene oxide and the partial oxidation of methanol to formaldehyde. Extensive investigations[1] have been performed in order to explore the mechanisms of these catalytic reactions and the characteristics of the catalyst. However, the reaction mechanism and the nature of the surface remain unanswered[2,3]. Fundamental studies in UHV system are more important for this solution.

Among gases, oxygen is the only one which chemisorbs on clean silver surfaces[1]. But the behavior of oxygen adsorption on silver is rather complex[3]. Water and hydrogen are usually the byproducts or impurities of the catalytic reaction on silver[4]. The roles of these gases are still unknown[5]. It has been tried in this work to elucidate the effects of oxygen pre-adsorption on the adsorptions of water and hydrogen in a UHV system.

EXPERIMENTAL

The experiment was conducted in a UHV chamber equipped with a quadrupole mass spectrometer (Anelva, AGA-100). The chamber was pumped by a UHV triode ion pump(Anelva, 110 *l*/s) lowering its background pressure to about 4×10^{-9} Torr. The main components of the residual gas were CO and H_2.

The 2.442 cm × 1.050 cm (× 0.035 cm thick) silver ribbon (99.999% in purity) was supported by and heated via two Ta-wires of 0.025 cm diameter. Temperature was measured by a chromel-alumel thermocouple spot-welded to the center of sample. The sample was reacted with $O_2(1 \times 10^{-6}$ Torr) and heated to 800 K to get rid of the surface impurities[6]. Oxidation and annealing procedures were repeated until the peaks of contaminants reached steady-state minima. Hydrogen and water gas were employed with high purity D_2(Fluka, 99.8%) and D_2O(Fluka, 99.8%), respectively. All the gases(O_2, D_2, CO) except D_2O were purified by passing through a liquid nitrogen trap.

RESULTS AND DISCUSSION

1. O_2 TDS

Figure 1 shows O_2 TDS spectra at various O_2 exposures. Three different adsorption states of oxygen species (α, β_1, and β_2 peak) are observed during desorption of oxygen. Figure 2 shows O_2 TDS spectra after exposing a 3600 L O_2-covered surface to CO of 0 L and 7200 L. It shows that the peak at 600 K disappears after reacting with CO. A number of experiments[7] have proven that CO can react with atomic oxygen on a

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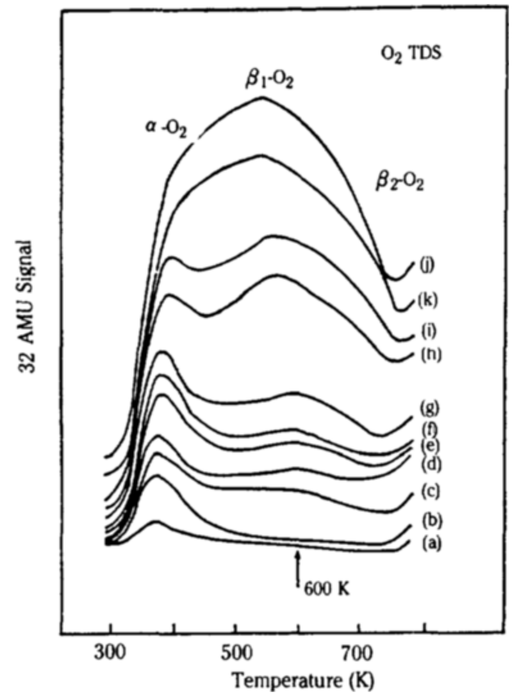

Fig. 1. Thermal desorption spectra of O_2 after the exposures of (a) 1 L, (b) 10 L, (c) 60 L, (d) 90 L, (e) 300 L, (f) 600 L, (g) 1200 L, (h) 3600 L, (i) 7200 L, (j) 10800 L, and (k) 18000 L.

silver surface to form CO_2 at room temperature, but not with molecular oxygen. Therefore, it may be concluded that the peak at low desorption temperature(α) corresponds to molecular oxygen and the peak at high temperature(β_1) to atomic oxygen. These show good agreements with decomposition temperatures of Ag_2O and Ag_2O_2[8] and previously published results[9].

In Fig. 1, with the increase of oxygen exposure from 1 L to 18000 L, the intensity of β_1 peak of 600 K increases and T_p(peak temperature) shifts toward lower temperature of about 540 K suggesting a second-order desorption kinetics, that is, recombination reaction according to the thermal desorption theory. The shift of T_p suggests strong repulsive lateral interactions between oxygen atoms on the surface which have negative charge[5]. The activation energy of desorption is 130 kJ/mole from Redhead's equation showing a good agreement with the results measured by different research groups[1].

The α peak at 385 K shifts slightly to higher temperature as the exposure increases. The α peak is overlapped by β_1 peak when the exposure is greater than 7200 L. The first-order activation energy is 97 kJ/mole by assuming 10^{13}/s of pre-exponential factor[2,7]. This phenomenon is also observed on an electrolytic catalyst in UHV system by Xinhe et al.[11] and in high pressure experiments[2,7]. It is commonly accepted that atomic oxygen exists on silver surface. However, it is disputable whether molecular oxygen exists on silver surface or not. Published results often depend on experimental conditions and systems. Especially, molecular oxygen is not observed in the 300-500 K range for single crystal silver in UHV system[12].

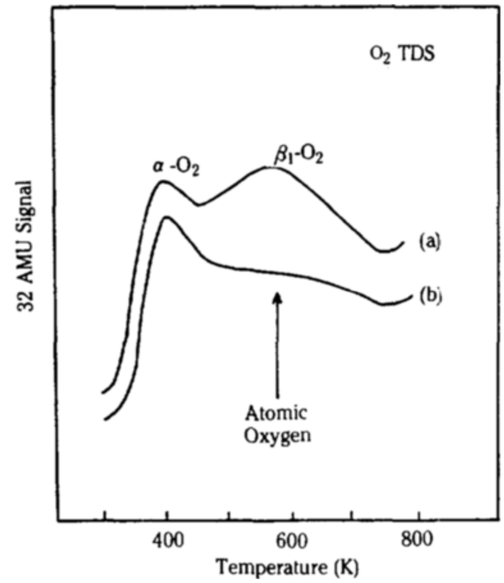

Fig. 2. Thermal desorption spectra of O_2 after exposing a 3600 L O_2-covered surface to CO of (a) 0 L and (b) 7200 L.

The diffusion of oxygen into the bulk of silver crystal was reported in a previous work[13]. By comparing our result with others, it is concluded that the desorption peak above 750 K is due to atomic oxygen diffusing into the bulk of silver.

2. Interaction between D_2O and O_2

Water adsorbed on the oxygen-dosed surface shown a maximum desorption rate at 430K and follows first-order desorption kinetics. This is not consistent with the results of single crystal experiments[1]. But the electrolytic catalyst[11] shows the D_2O TDS spectra giving maximum desorption rates at 410 and 450 K.

Figure 3 shows the effect of the coverage of surface oxygen species on the amount of adsorbed D_2O in a given range of pre-adsorbed oxygen coverage. Small adsorption of D_2O occurs on a clean surface. However, the adsorption of water on an oxygen-dosed surface is strongly dependent on the amount of pre-adsorbed oxygen. The amount of water adsorbed is proportional to that of pre-adsorbed oxygen, but the amount de-

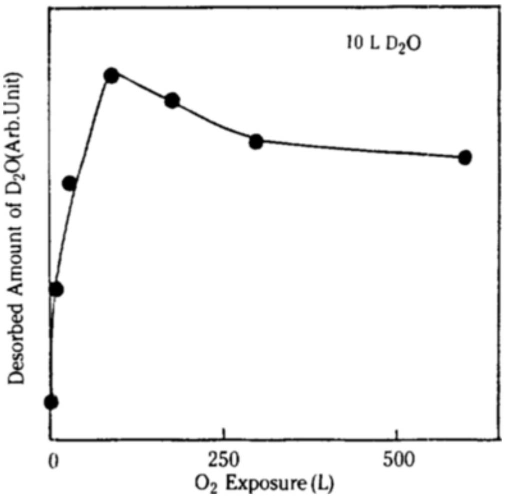

Fig. 3. **Effect of pre-adsorbed O_2 on the adsorption of D_2O. The exposure of D_2O is 10 L.**

creases at higher than 100 L oxygen exposures. This indicates water molecules interact strongly with pre-adsorbed oxygen atoms. The origin of this induced adsorption is attributed to the electronegativity of the oxygen adatoms. The oxygen adatoms have higher basicity, and so strip adjacent water molecules of their protons, presumably resulting in the formation of a pair of hydroxyl species[OD(a)]. Therefore, the higher oxygen coverage results in the inhanced water adsorption. The formation of hydroxyl group on the single crystal silver has been studied by both isotopic exchange and EELS experiments[14]. The hydroxyl groups, in turn, would be expected to interact as strong bases with neighboring water molecules. The decrease of the amount of water adsorbed at still higher oxygen exposure is explained by weakening the basicity due to the repulsive interaction between pre-adsorbed oxygen and by adsorption site blocking by pre-adsorbed oxygen.

3. Interaction between D_2 and O_2

Figure 4 shows D_2 TDS spectra at various D_2 exposure on the pre-adsorbed oxygen. Hydrogen desorbs at 470 K. By comparing QMS sensitivity of hydrogen with those of other gases, the amount of hydrogen desorbed is very small. This does not agree with the previous single crystal results[15], in which no hydrogen desorption peak was observed at this temperature range.

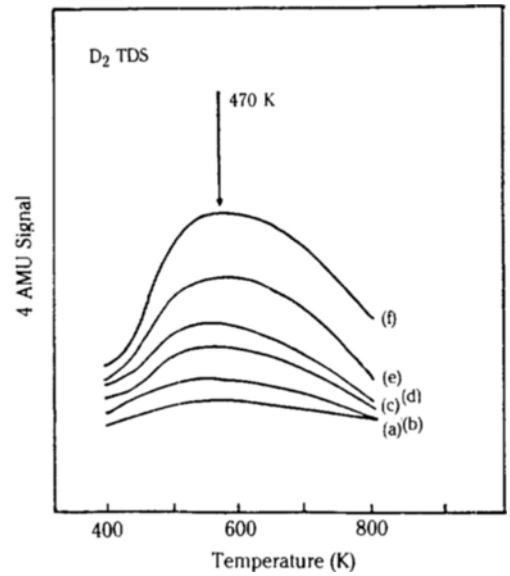

Fig. 4. **Thermal desorption spectra of D_2 after exposing a 30 L O_2-covered surface to D_2 of (a) 30 L, (b) 60 L, (c) 90 L, (d) 120 L, (e) 180 L, and (f) 360 L.**

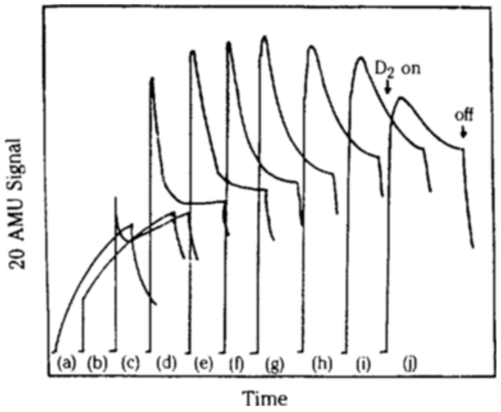

Fig. 5. **D_2O spectra produced from D_2 reaction (D_2 pressure of 1×10^{-6} Torr) at 300 K with pre-adsorbed O_2 of (a) 0 L, (b) 10 L, (c) 30 L, (d) 90 L, (e) 180 L, (f) 240 L, (g) 360 L, (h) 600 L, (i) 1200 L, and (j) 1800 L.**

Figure 5 shows D_2O spectra produced from D_2 reaction(D_2 pressure of 1×10^{-6} Torr) at 300 K with various amounts of pre-adsorbed O_2. The time origin refers to the point at which D_2 gas valve turns on. D_2 is observed to react with adsorbed oxygen on the silver surface at 300 K. The D_2O signal exhibits a sharp rise followed by a typical first-order decay. The curves show that the active oxygen is depleted from surface during its exposure to D_2. Comparing curve (e) with curve (i) of Fig. 5, both of which show the same amount of D_2O produced at the time zero, (e) is faster than (i) in depletion rate of active oxygen. The peak height is proportional to the rate of water formation. The

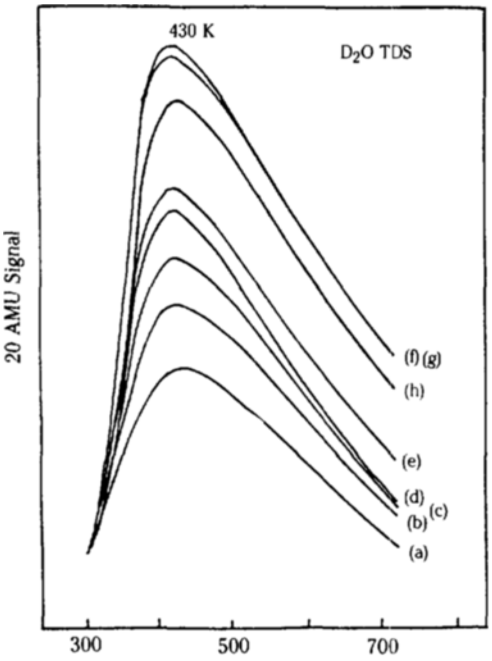

Fig. 6. Thermal desorption spectra of D_2O after D_2-titration in Fig. 5 (Assignments of (a) to (h) are same as those in Fig. 5).

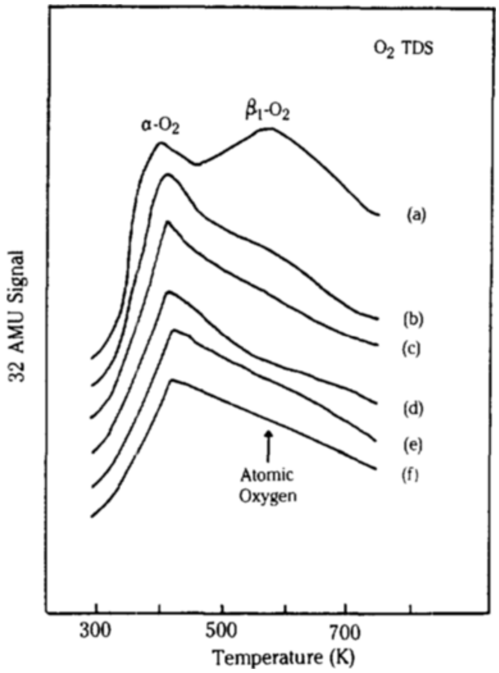

Fig. 7. Thermal desorption spectra of O_2 after exposing a 3600 L O_2-covered surface to D_2 of (a) 0 L, (b) 1800 L, (c) 2400 L, (d) 3000 L, (e) 3600 L, and (f) 4320 L.

difference in depletion rate with different pre-exposure of O_2 and the maintenance of the water formation rate after sharp decrease suggest a reaction with bulk atomic oxygen diffusing to the surface. This allows the possibility of distinguishing surface active oxygen from bulk one. The result is different from the single crystal result in which hydrogen did not react with adsorbed oxygen atom on silver surface due to its low acidity[16]. But this is consistent with that of high pressure reaction[17,18]. The result supports the previous works[4,5] that hydrogen is harmful for catalytic reaction over silver and that hydrogen titration technique is used to the surface area estimation of supported silver catalyst.

After these experiments, small amount of D_2O is left on the surface(Fig. 6): the amount of D_2O remaining is approximately 7% as seen by comparison of D_2O spectra in Fig. 5. All of the residual D_2O desorbs at around 430K. It is the same as the result of D_2O TDS spectra after D_2O exposure on pre-adsorbed oxygen surface. This indicates indirectly that the rate-determining step for the D_2 oxidation is the desorption of product D_2O.

In Figs. 5 and 6, hydrogen oxidation on the oxygen-dosed surface and adsorption of water after the reaction are strongly dependent on the amount of pre-adsorbed oxygen. The amount of produced D_2O is proportional to that of pre-adsorbed oxygen, but the amount decreases at higher oxygen exposure. This is explained by that the increase of negatively charged oxygen increases the adsorption of D_2 and then production of D_2O, but at higher exposure, the adsorption of D_2 decreases because of repulsive lateral interaction between charged oxygens.

The adsorbed amount of D_2 in D_2 oxidation is around 5% (Fig. 4). Our other result shows that the desorption of D_2 increases as pre-adsorbed oxygen increases and that D_2 does not adsorb on a clean surface. Small amount of D_2 desorption indicates that the reverse reaction of D_2 oxidation, D_2 formation from D_2O, is very slow.

Figue 7 shows O_2 TDS spectra after various D_2 exposures on 3600 L O_2-covered surface. With curve fitting, only atomic oxygen peak(β_1 peak) disappears after reacting with D_2. It suggests that D_2 reacts only with atomic surface oxygen[O(a)] in D_2 oxidation on silver surface. Figure 8 shows D_2O and DHO spectra produced from D_2 reaction(D_2 pressure of 1×10^{-6} Torr) at 300 K with pre-adsorbed 90 L O_2. We can understand that DHO spectrum is produced by background H_2, and that hydrogen adsorbed on pre-adsorbed oxygen is dissociated. The following reaction scheme

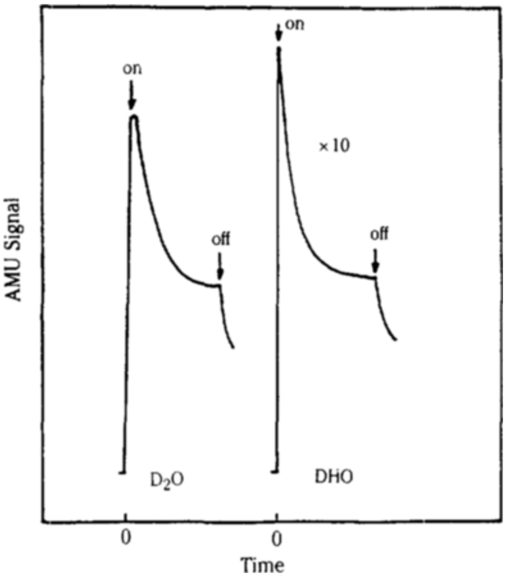

Fig. 8. D_2O and DHO spectra produced from D_2 reaction(D_2 pressure of 1×10^{-6} Torr) at 300 K with pre-adsorbed 90 L O_2.

is suggested from the results:

$$H_2+2O(a)\rightarrow 2OH(a)\rightarrow H_2O+O(a)$$

$$D_2+2O(a)\rightarrow 2OD(a)\rightarrow D_2O+O(a)$$

$$OH(a)+OD(a)\rightarrow DHO+O(a)$$

When a pre-adsorbed 1200 L O_2 reacts with D_2 of 1×10^{-6} Torr for 40 sec at different substrate temperatures, the amount of D_2O produced increases as the substrate temperature increases to 600 K at which atomic oxygen desorbs, and then decreases at higher temperatures. But the amount increases again when the bulk oxygen desorbs. The result is shown in Fig. 9. This temperature effect is more distinctive at smaller amount of pre-adsorbed oxygen. Haruta et al. [19] suggested that the breaking of metal-oxygen(M-O) bond was the slowest step in hydgrogen oxidation over oxides. From this suggestion, the decrease of bond energy by the increase of substrate temperature increases D_2O production suggesting that D_2O desorption is the slowest step in D_2 oxidation on silver catalyst.

The following mechanism is proposed from the experimental data:

$$1/2O_2\rightarrow O(a)$$

$$O(a)+1/2H_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} OH(a)$$

$$OH(a)+1/2H_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} H_2O$$

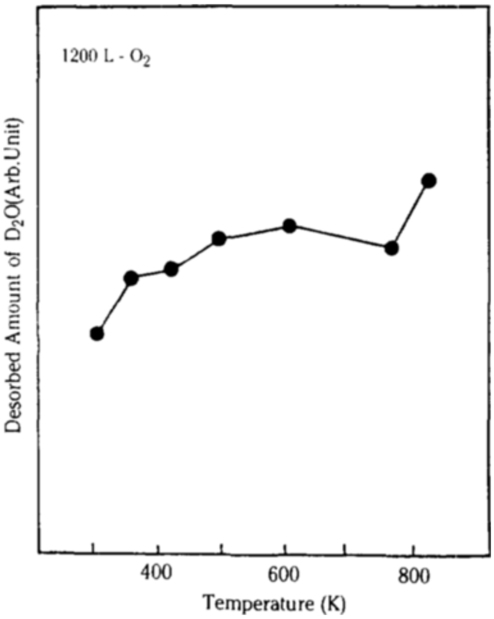

Fig. 9. Effect of substrate temperature on the desorption of D_2O in the case of 1200 L O_2.

Hydrogen reacts first with O(a) to yield hydroxyl intermediate and then water is produced by further reaction of the intermediate. The rate-determining step in this reaction is desorption of water. The mechanism of hydrogen oxidation on silver catalyst is little known. It is agreed with several postulated mechanisms derived from reaction kinetics at about 10^{-2} Torr[17,18].

The rate equation has been derived from to the above proposed mechanism. Assuming the steady-state for OH(a) when [O(a)] is the amount of oxygen left on the surface after reaction time t;

$$d[OH(a)]/dt=0=k_1[H_2]^{1/2}[O(a)]-k_2[OH(a)]$$
$$-k_3[OH(a)][H_2]^{1/2}+k_4[H_2O]$$

and

$$[OH(a)]=\frac{k_1[H_2]^{1/2}[O(a)]+k_4[H_2O]}{k_2+k_3[H_2]^{1/2}}$$

Because water formation rate is equal to oxygen-depletion rate from steady-state approximation,

$$\begin{aligned} d[H_2O]/dt &= -d[O(a)]/dt \\ &= k_1[O(a)][H_2]^{1/2}+k_2[OH(a)] \\ &= \frac{k_1k_3[H_2][O(a)]+k_2k_4[H_2O]}{k_2+k_3[H]^{1/2}} \\ &= k_1[H_2]^{1/2}[O(a)]=k'[O(a)]. \end{aligned}$$

The terms containing k_2 are omitted because the reverse reaction is slow from the result of Fig. 4. Finally, the reaction shows a first-order kinetics at a constant hydrogen pressure.

From an Arrhenius plot, the activation energy for the reaction of D_2 with adsorbed oxygen over the temperature range of 310 to 821 K is 1.44 kJ/mole with pre-exponential factor 2.03×10^{-3}/s. This small value is similar to 2.5 kJ/mole of CO oxidation on silver catalyst by Albers et al.[20]. It is suggested that D_2 oxidation on silver surface is very fast.

CONCLUSIONS

1. Three states of adsorbed oxygen species are observed on the surface: (a) adsorbed molecular oxygen(E_d=97 kJ/mole, T_p=385 K), (b) adsorbed atomic oxygen(E_d=130 kJ/mole, T_p=600 K), and (c) bulk atomic oxygen(T_p is higher than 750 K).

2. Water on the oxygen-dosed surface shows a maximum desorption rate at 430 K. The amount of adsorbed gases is proportional to the pre-adsorbed oxygen, but at higher oxygen exposures the amount decreases.

3. During the adsorption of hydrogen on the oxygen-dosed surface, hydrogen is rapidly oxidized to water. Remaining water on the surface (7%) desorbs at 430 K and a small amount of hydrogen does at 470 K. The adsorption and reaction of hydrogen on the oxygen-dosed surface are strongly dependent on the amount of pre-adsorbed oxygen.

4. The mechanism of water formation is shown to be a stepwise reaction in which hydrogen reacts first with O(a) to yield hydroxyl group[OD(a)] intermediate and then water is produced by a further reaction of this intermediate. The rate-determining step is desorption of water. The kinetics of hydrogen oxidation at a constant hydrogen pressure over the temperature range of 310 K to 821 K shows a first-order in the concentration of O(a) and the activation energy is 1.44 kJ/mole.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Korea Science and Engineering Foundation for this work.

NOMENCLATURE

EELS : electron energy loss spectroscopy
k_1, k_2, k_3, k_4, k' : rate coefficient of the corresponding reaction
L : a unit of gas exposure, Torr·sec
O(a), OD(a), OH(a) : surface state of the corresponding species
TDS : thermal desorption spectroscopy
UHV : ultra-high vacuum
$[H_2]$, [O(a)], [OH(a)] : concentration of the corresponding species
α, β_1, β_2: name of the corresponding peak in thermal desorption spectrum of oxygen

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