Detection of radical species produced by catalytic decomposition of H₂, O₂ and their mixtures on heated Ir surfaces

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Efficient production of H atoms, O atoms and OH radicals was confirmed by laser spectroscopic measurements in the catalytic decomposition of H₂, O₂ and their mixtures on a heated Ir filament. No change in electric resistivity was observed when the filament was kept at 2350 K in the presence of 1.0 Pa of pure O₂, showing that oxidation is minor. Arrhenius-type temperature dependences were observed for the densities of H (O) atoms in pure H₂ (O₂) systems. In the H₂/O₂ mixed system, the H-atom density was almost independent of the O₂ partial pressure, although the O-atom and OH-radical densities increased with the O₂ pressure. These O₂ pressure dependences are completely different from those observed for W. Ir is less poisoned by O₂ compared to W. In addition, direct production of H₂O molecules on Ir surfaces must take place besides the production of radical species.

Keywords: Catalytic chemical vapor deposition, Hot-wire chemical vapor deposition, Iridium, Oxygen, Hydrogen, Atomic oxygen, Atomic hydrogen, OH radical

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1. Introduction

Catalytic decomposition of oxidizing species, such as O_2 , on heated metal filaments has been paid less attention compared to that of reducing species, such as H_2 and SiH_4 , because of the oxidization and the breaking of the filaments. Recently, we have shown that oxidization of W, one of the most widely used materials in catalytic CVD processes, can be diminished by the addition of an excess amount of H_2 or NH_3 [1] and that H atoms, O atoms and OH radicals are produced in the catalytic decomposition of H_2/O_2 mixtures [2]. However, pure O_2 cannot be introduced to produce atomic oxygen as far as W is used. In addition, it was found that the production rate of H atoms decreases rapidly by the introduction of more than 0.3% of O_2 and the co-production of high-density H and O atoms is rather difficult [2]. On the other hand, Ir has high oxidation durability [3-5]. Saito *et al.* have shown that Ir is not oxidized even when it is heated in pure O_2 atmosphere and that Ir catalysts can be used to prepare SiO_2 films [3]. Ogita and Tomita have also used Ir catalysts to prepare Al_2O_3 films from $Al(CH_3)_3$ and O_2 [4]. Wu *et al.* have recently reported that the electrical and optical properties of indium-tin oxide films can be improved by the radical treatment produced by the catalytic decomposition of O_2 on heated Ir catalysts. The improvement in electric resistivity was much better than that after an oxygen plasma treatment [5].

In the oxidation processes of Wu *et al.*, the only radical species expected is ground-state atomic oxygen, but the identification or quantification of such species has not been carried out. The production efficiency of atomic hydrogen on heated Ir surfaces has not been reported, either. In the present work, absolute densities of H atoms, O atoms and OH radicals were determined by laser spectroscopic techniques in the catalytic decomposition of H_2 , O_2 and their mixtures on heated polycrystalline Ir surfaces. In addition, the consumption efficiencies of O_2 in the H_2/O_2 mixtures were

measured by using a quadrupole mass spectrometric technique and the possible decomposition mechanism is discussed.

2. Experimental Details

The experimental apparatus and the procedure were similar to those described elsewhere, except for the catalyzer materials and sizes [2]. An Ir wire (Tanaka Precious Metals, 30 cm in length and 0.50 mm in diameter, 99.9%) was used instead of W. The catalyzer temperature was estimated from the relationship between the resistivity and the temperature [6]. Radical species produced on the heated catalyzer were detected in three systems, pure H₂, pure O₂ and their mixtures. The flow rate of H₂ was fixed at 100 sccm (1 sccm = 6.9×10^{-7} mol s⁻¹) by using a mass flow controller (STEC, SEC-400MK3), and the pressure was kept at 17 Pa otherwise stated. The flow rate of O₂ was changed between 0.00 and 1.20 sccm by using another mass flow controller (STEC, SEC-7320M). The inner walls of the chamber were coated with SiO₂ in order to reduce the removal rates of radical species [7].

Three laser spectroscopic techniques were employed to measure the H-atom densities. The first one was the vacuum-ultraviolet (vuv) laser absorption technique at 121.6 nm, Lyman- α . By this technique, it is possible to determine the absolute densities. The second one was the vacuum-ultraviolet laser-induced fluorescence (vuv LIF) at 121.6 nm. This technique is more sensitive, but cannot be employed when the H-atom density is high because the vuv laser beam can easily be absorbed by H atoms not to reach the central part of the chamber. The third one was two-photon LIF at 205.1 nm to excite to H(3s ²S, 3d ²D) and to observe Balmer- α at 656.3 nm. This technique is less sensitive, but can be used in the presence of an excess amount of H atoms. The relative values obtained by LIF techniques were scaled to the absolute ones by comparing the signal intensities where the absolute values are available from

the absorption technique.

O atoms were detected by a vuv LIF technique at 130.2 nm. The absolute values were evaluated from absorption measurements, the details of which will be presented elsewhere [8]. OH radicals were detected by employing an LIF technique in the ultraviolet region. The absolute densities were evaluated by comparing the time integrated LIF intensity for the $P_1(N''=2, J''=3/2)$ transition at 308.6 nm under saturated conditions with the intensity of Rayleigh scattering caused by Ar. Mass spectrometric analysis was also carried out to determine the consumption efficiency of O_2 in H_2/O_2 mixed systems.

3. Results

The catalyzer temperature dependence of the H-atom density in a pure H_2 system is shown in Fig. 1. The logarithm of the H-atom density has a linear dependence on the reciprocal of the catalyzer temperature. The apparent activation energy determined from the slope is 295 kJ mol^{-1} , which is a little larger than that obtained for W in our previous study, 239 kJ mol^{-1} [9]. The result for W has been confirmed in our recent study, in which exactly the same apparatus was used [10], and is consistent with the results obtained by other investigators [11]. The absolute H-atom density may seem less than those obtained when W is used [9], but this difference should be ascribed to the difference in the chamber size. When a small chamber is used, H atoms are removed more rapidly by recombination processes on chamber walls. The H-atom density obtained by using an Ir filament, $1 \times 10^{13} \text{ cm}^{-3}$ at 2200 K, was comparable to that when the same chamber was used with a W filament [10].

The H-atom density increased with the H_2 pressure but the increase was rather gradual over 10 Pa. This dependence is similar to that observed when W was used as a catalyzer [9]. The two-photon LIF signal increased by just 25% when the pressure was

increased from 10 Pa to 17 Pa at 2200 K. Quenching of excited H atoms by H₂ cannot completely be ignored under the present conditions, but that cannot be the main cause of the saturation because of the short radiative lifetimes of the upper states [12].

The O-atom density also showed an Arrhenius-type temperature dependence and the apparent activation energy was determined to be 260 kJ mol⁻¹, which is a little smaller than that for the H-atom production process. The O₂ flow rate dependence of the O-atom density in a pure O₂ system at the catalyzer temperature of 2100 K is plotted in Fig. 2. Similar dependences were observed at other temperatures. When the catalyzer temperature was increased up to 2350 K in the presence of 1.0 Pa of pure O₂, at the flow rate of 1.20 sccm, the O-atom density increased up to 2×10^{12} cm⁻³.

The O₂ flow rate dependences of the H-atom density between 1700 and 2200 K in H₂/O₂ mixed systems are plotted in Fig. 3. At all temperatures, the H-atom densities depend little on the O₂ flow rate. It should be noted that such a behavior is completely different from that observed when W was used a catalyzer. In the case of W, the H-atom density decreases stepwisely [2]. In other words, Ir is less poisoned by O₂ than W. The O₂ flow rate dependence of the O-atom density in the presence of an excess amount of H₂ was similar to that for W. The rise of the O-atom density was faster than linear. The absolute density was around 1/50 of that in pure O₂ systems, in the order of 10¹⁰ cm⁻³ at 2100 K, which is the same order as that for W.

The LIF spectrum of OH(X ²Π, *v*"=0) was similar to that obtained when W was used and the rotational temperature was around 350 K [2]. On the other hand, the O₂ flow rate dependence of the OH density was different from that observed for W. Fig. 4 shows that the OH-radical density increases nonlinearly against the O₂ flow rate. In the case of W, the OH density saturates [2]. The OH signal at the catalyzer temperature of 2200 K was around twice as intense as that at 2100 K.

The H₂ pressure dependences of the radical densities were also examined.

The O_2 partial pressure and the H_2 flow rates were kept constant at 0.17 Pa and 100 sccm, respectively. The catalyzer temperature was 2200 K. In these measurements, since the diffusion coefficients of radicals, and consequently the removal rates, may change, quantitative analyses are difficult, but qualitative discussion may still be possible. The OH-radical density decreased by a factor of 4 when the H_2 pressure was increased from 17 to 34 Pa. This dependence is again opposite to that observed for W [2]. The O-atom density also decreased by a factor of 4. The H_2 pressure dependence of the H-atom density in the presence of a fixed amount of O_2 was similar to that observed in pure H_2 systems.

According to quadrupole mass-spectrometric measurements, the consumption efficiency of O_2 was 43%, independent of the catalyzer temperature over 1100 K. The flow rates of H_2 and O_2 were 100 and 1.00 sccm, respectively. This consumption efficiency is much larger than that for W, 16% at 2000 K [2]. The independence of the consumption efficiency is in contrast to the large activation energies observed for the production of O and OH.

4. Discussion

According to mass spectrometric measurements in the H_2/O_2 mixed systems, when the catalyzer temperature is between 1100 and 1500 K, O_2 is consumed efficiently, although the radical production is inefficient. This contradiction can be accounted for by the efficient production of H_2O molecules on catalyzer surfaces without producing radical species at such moderate temperatures. The production of H_2O could also be confirmed mass spectrometrically. This conclusion is consistent with the result of the H_2 and O_2 pressure dependences of the OH radical densities. The ejection of OH radicals may compete with that of H_2O molecules. The production of OH should be more efficient at lower H_2 pressures and at higher O_2 pressures.

The production rate of H atoms is not affected by the addition of O₂. The interaction between Ir and O atoms must be weaker than that between W and O atoms and the residence time of O atoms on Ir must be shorter. According to Krekelberg *et al.*, the binding energy of O atoms on Ir surfaces is larger than that for H atoms, but the difference is not great [13]. The binding energy of H atoms on W surfaces is also comparable [14]. However, judging from the bond energies of WO and IrO diatoms [15], the binding energy of O atoms on W surfaces must be much larger. The residence time of O atoms on Ir surfaces must be much shorter than that on W surfaces. The observed activation energy for H₂ is comparable to the Ir-H binding energy calculated by Krekelberg *et al.*, while that for O₂ is smaller than the calculated energy. This point will be discussed elsewhere together with the data on nitrogen oxide molecules [8].

The minor H₂ pressure dependence of the H-atom density over 10 Pa suggests that the nonlinear increase in the recombination rate of H atoms against the H-atom densities on chamber walls. The production rate of H atoms must increase with the increase in the H₂ pressure [11]. The diffusion rate must decrease to lower the recombination rate of H atoms on chamber walls. Three-body recombination processes in the gas phase must be minor under the present low-pressure conditions. On the other hand, the H-H atom recombination rate on chamber walls may increase with the square of the surface density of H atoms.

Similar explanation may be possible for the saturation of the O-atom density against the O₂ pressure. However, the shortage of the active sites on catalyzer surfaces should be a more probable explanation to this saturation, because the pressure ranges are different. As for H atoms, the saturation could only be observed when the H-atom density is in the order of 10¹³ cm⁻³. The residence time of O atoms on Ir surfaces may be shorter than that on W surfaces, but must be longer than that of H atoms. When the

O₂ pressure is higher than 1 Pa, Ir surfaces may completely be covered with O atoms in the absence of an excess amount of H₂. In other words, the O-atom density may be increased to more than 10¹² cm⁻³ just by increasing the catalyzer length. In addition, judging from the chamber size dependence of the H-atom densities, the O-atom density may also be increased by one order by using a larger chamber, in which the atom recombination processes on chamber walls are less important.

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References

- [1] H. Umemoto, S. G. Ansari, T. Morimoto, S. Setoguchi, H. Uemura, H. Matsumura, *Thin Solid Films* 516 (2008) 829.
- [2] H. Umemoto, M. Moridera, *J. Appl. Phys.* 103 (2008) 034905.
- [3] K. Saito, Y. Uchiyama, K. Abe, *Thin Solid Films* 430 (2003) 287.
- [4] Y. Ogita, T. Tomita, *Thin Solid Films* 501 (2006) 35.
- [5] D.-S. Wu, S.-Y. Lien, H.-Y. Mao, J.-H. Wang, B.-R. Wu, P.-C. Yao, I.-C. Hsieh, H.-H. Peng, R.-H. Horng, Y.-C. Chuang, *Thin Solid Films* 501 (2006) 346.
- [6] R.T. Wimber, J.J. Halvorson, *J. Mater.* 7 (1972) 564.
- [7] S.G. Ansari, H. Umemoto, T. Morimoto, K. Yoneyama, A. Masuda, H. Matsumura, M. Ikemoto, K. Ishibashi, *J. Vac. Sci. Technol. A* 23 (2005) 1728.
- [8] H. Umemoto, H. Kusanagi, *J. Phys. D: Appl. Phys.* 41 (2008) 225505.
- [9] H. Umemoto, K. Ohara, D. Morita, Y. Nozaki, A. Masuda, H. Matsumura, *J. Appl. Phys.* 91 (2002) 1650.
- [10] M. Yamamoto, H. Umemoto, H. Horibe, T. Miura, E. Kusano, S. Tagawa, unpublished if not accepted for publication.
- [11] W. Zheng, A. Gallagher, *Surf. Sci.* 600 (2006) 2207.
- [12] J. Bittner, K. Kohse-Höinghaus, U. Meier, *Th. Just, Chem. Phys. Lett.* 143 (1988) 571.
- [13] W.P. Krekelberg, J. Greeley, M. Mavrikakis, *J. Phys. Chem. B* 108 (2004) 987.
- [14] K. Christmann, *Surf. Sci. Rep.* 9 (1988) 1.
- [15] K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York NY, 1979.

List of Figure Captions

Fig. 1 H-atom density as a function of the reciprocal of the catalyzer temperature measured by a vacuum-ultraviolet laser absorption technique ($\circ$), a two-photon laser induced fluorescence technique ($\bullet$) or a one-photon laser induced fluorescence technique ($\blacktriangle$). The H_2 flow rate was 100 sccm and the pressure was 17 Pa. The absolute values were evaluated from the absorption technique.

Fig. 2 O-atom density as a function of O_2 flow rate in a pure O_2 system. The catalyzer temperature was 2100 K. The O_2 pressure was 1.0 Pa when the flow rate was 1.20 sccm.

Fig. 3 H-atom densities as a function of O_2 flow rate measured by a two-photon laser induced fluorescence technique (open symbols) and a one-photon laser induced fluorescence technique (closed symbols). The H_2 flow rate was 100 sccm and the total pressure was 17 Pa. The catalyzer temperatures were 2200 K ($\circ$), 2100 K (Δ), 2050 K ($\square$), 1850 K ($\bullet$), and 1700 K ($\blacktriangle$).

Fig. 4 OH-radical densities as a function of O_2 flow rate. The H_2 flow rate was 100 sccm and the total pressure was 17 Pa. The catalyzer temperatures were 2200 K ($\circ$) and 2100 K ($\bullet$).

Fig. 1

Fig. 2

Fig. 3

Fig. 4