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Jansen et al. have demonstrated that the dissociaiton rate of H_2 molecules on hot wire surfaces, normalized per unit surface area, depends on the wire diameter based on the electrical power consumption measuremnents [J. Appl. Phys. **66**, 5749 (1989)]. Mathematical modeling calculations have also been presented to support their experimental results. In the present paper, it is shown that such a wire diameter dependence cannot be observed and that the H-atom density normalized by the wire surface area depends little on the wire diameter. Modeling calculations also show that the wire diameter dependence of the dissociation rate cannot be expected under typical decomposition conditions.

1. Introduction

Jansen et al. have reported that the decomposition efficiency of H_2 molecules on heated metal wires, normalized per unit surface area, depends on the wire geometry.[1] They have concluded, from the wire temperature dependence of the electrical power consumed, that the decomposition efficiency is larger for small-diameter wires when the H_2 pressure is high, such as 4.7 kPa, and the mean-free-path is smaller than the wire diameter. To explain their results, they proposed a mathematical model. They solved diffusion equations for H_2 molecules and H atoms numerically and attributed their results on the wire-diameter dependence to the non-equilibrium nature of the dissociation process in the vicinity of the wire. They could reproduce their experimental results by numerical calculations under some conditions, such as when the $[H]/[H_2]$ population ratio exceeds 10%. It should be remembered that, in the catalytic decomposition processes of diatomic species on hot wire surfaces, the atomic density does not increase linearly against the pressure of parent molecules.[2-6] The typical $[H]/[H_2]$ ratio is less than 1% when the H_2 pressure is more than 1 kPa. It is desired to check if the wire-diameter dependence of the H-atom densities can be observed under small $[H]/[H_2]$ conditions.

In the present study, besides the power consumption measurements, the H-atom densities were measured as functions of wire diameter as well as wire temperature by using a two-photon laser-induced fluorescence technique. Numerical modeling calculations similar to those by Jansen et al. were also carried out to evaluate the H-atom densities as a function of wire diameter.

2. Experimental procedure

The experimental procedure and apparatus were similar to those described elsewhere.[3,4,7-9] H_2 was decomposed catalytically on a resistively heated W wire installed in a cylindrical chamber evacuated by a turbomolecular pump (Osaka Vacuum TG220FCAB). Gas flow rates were controlled by a mass flow controller (Horiba STEC SEC-40M). The inner walls of the chamber were coated with SiO_2 to reduce the removal rates of radical species.[10] The distance between the wire and the laser beam detection zone was 9 cm. The wire diameter was changed between 0.2 and 0.6 mm.

The wire temperature was measured with a two-wavelength thermometer (LumaSense Technologies ISR 12-LO). When the wire diameter was less than 0.4 mm, the measured temperature agreed with that evaluated from the electrical resistivity.[11] On the other hand, when the wire diameter was 0.6 mm and the wire length was 30 cm, the temperatures evaluated from the resistivity were 10–20% higher than those measured with a thermometer. Temperatures evaluated with a thermometer are more reliable because the observed temperature depended little on the diameter under vacuum when the electrical power and the surface area were fixed. When the wire is thick and short, the contact resistance at terminals may not be ignored.

The H-atom densities were evaluated by a two-photon laser-induced fluorescence (LIF) technique at 205.1 nm.[2,6,7,9,12] A dye laser (Sirah CSTR-LG-18) pumped with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Quanta-Ray GCR-170) was used as a light source. The frequency of the dye laser output at 615.3 nm was tripled by using two β-BaB_2O_4 (BBO) crystals and a polarizer. The resulting radiation was focused with a 150-mm focal-length lens. The Balmer-α fluorescence at 656.3 nm was detected with a photomultiplier tube (Hamamatsu Photonics R212UH) through an interference filter (Nihon Shinku Kogaku). The photomultiplier signals were processed with a digital oscilloscope (LeCroy 6051A).

The absolute H-atom densities were not evaluated because information on the relative densities is sufficient for the present purpose. In any case, it is difficult to determine the absolute densities in the presence of more than 1 kPa of H_2, because the quenching processes of the two-photon excited upper states cannot be ignored.[6] The radiative lifetimes of H(3s ^2S), H(3p ^2P_J), and H(3d ^2D_J) states are fairly long, 158, 45, and 15 ns, respectively,[13] while the rate constants for the quenching by H_2 are extremely large; the rate constants are as large as 2×10^{-9} cm^3s^{-1}.[14-17] Unless the ratio of H(3s ^2S), H(3p ^2P_J), and H(3d ^2D_J) populations is known, it is impossible to correct the effect of quenching. The Lyman-α absorption technique cannot be employed, either, because the transmittance shall be too low to evaluate the absolute densities.

H_2 (Japan Air Gases, 99.999%), D_2 (Sumitomo Seika, isotopic purity 99.5%), and He (Japan Air Gases, 99.999%) were used from cylinders without further purification.

3. Results and discussion

The present experimental results were in contradiction to those of Jansen et al.[1] Figure 1 shows the dependences of electrical power consumed on catalyst temperature measured in vacuum and in the presence of H_2, D_2, and He. The wire lengths and diameters were 40 cm and 0.3 mm or 30 cm and 0.4 mm, respectively. The larger power observed for H_2 and D_2 can easily be explained by the power consumption required to dissociate molecules.[18] The difference between H_2 and D_2 can be explained by the difference in collision frequencies. Below 2000 K, molecular dissociation is inefficient and the difference between D_2 and He is minor. These results are similar to those obtained by Jansen et al.,[1] but it should be noted that no diameter dependence was observed. The absence of the diameter dependence is also shown in Fig. 2. In Fig. 2, the relative H-atom densities divided by the surface area are plotted as a function of the reciprocal of wire temperature. No wire diameter dependence could be observed. The activation energy calculated from the slope of the plots in Fig. 2, 222 ± 5 kJ mol^{-1}, is consistent with the literature values.[6] In the present system, the mean-free-path is on the order of 10^{-2} mm, which is much smaller than the wire diameter. Judging from the present results, Jansen's mathematical model may not always be applied in the decomposition of H_2.

Jansen et al. have demonstrated that their experimental results are consistent with a mathematical model.[1] The present author followed their calculations by using a Runge-Kutta-Gill method and has succeeded in reproducing their calculated results. They assumed an infinite cylinder geometry and the following diffusion equations were solved numerically:

$$-D\left(\frac{d^2C_M}{dr^2}+\frac{1}{r}\frac{dC_M}{dr}\right)=-k_0\exp\left(\frac{r_0-r}{\alpha}\right)C_M, \qquad (1)$$

$$-D\left(\frac{d^2C_A}{dr^2}+\frac{1}{r}\frac{dC_A}{dr}\right)=2k_0\exp\left(\frac{r_0-r}{\alpha}\right)C_M. \qquad (2)$$

Here, r is the radial coordinate and r_0 is the wire radius. D is the diffusion coefficient and the same values were assumed for both H_2 and H. C_M and C_A represent the densities of H_2 and H, respectively. It was assumed that the decomposition takes place only in the gas phase and the rate constant, which is proportional to k_0, decreases exponentially with the distance from the wire surface. The length of the

decomposition region is represented by a parameter α. The recombination processes of H atoms were not included explicitly, but it was assumed that the H-atom density at the chamber walls is zero, $C_A(r=R)=0$, while the H_2 density asymptotes to a certain value, $C_M(r=R)=C_0$. Here, R is the cylinder radius. Their assumption of the thermal decomposition of H_2 in the gas phase is in contradiction to the results of more recent studies.[5,6,19-21] It has been shown that the catalytic decomposition on wire surfaces is the dominant source of H atoms and gas-phase reactions play only a negligible role. According to the present calculations, however, the spatial distributions of H_2 and H were found to depend little on the choice of the value of α. Surface reactions may correspond to the limit of α→0. The boundary conditions they employed,

$$\frac{dC_M}{dr}|_{r=r_0} = \frac{dC_A}{dr}|_{r=r_0} = 0\,, \qquad (3)$$

are also in contradiction to the catalytic decomposition model, but, fortunately, no large dependence was observed on the choice of the differentials of the densities, dC_M/dr and dC_A/dr, at $r=r_0$.

It was easy to reproduce the calculated results of Jansen et al. Figure 3 shows the calculated molecular and atomic hydrogen densities in the gas phase, normalized by the H_2 density at the chamber walls, C_0, along the radial direction, r. The boundary conditions were the same as those adopted by Jansen et al. The wire radius, r_0, and the decay length of decomposition, α, were both assumed to be $0.01R$. Jansen et al. have introduced the following K parameter, the integral of the reaction rate constant in the chamber volume,

$$K = \frac{1}{2\pi r_0}\int_0^{2\pi} d\theta \int_{r_0}^{\infty} k_0 \exp\left(\frac{r_0-r}{\alpha}\right) r dr \cong k_0\alpha(\frac{\alpha}{r_0}+1). \qquad (4)$$

The densities can be calculated for various values of KR/D. The results shown in Fig. 3 are those for KR/D = 1 and 10. Figure 3 shows that the $[H]/[H_2]$ population ratio, C_A/C_M, is small when KR/D is small. When KR/D=10, that ratio is 0.11 at $r=R/2$, while it is 0.013 when KR/D=1. The problem is that these ratios are too large, as will be shown below.

When the H_2 pressure is low and the quenching of excited H atoms can be ignored, it is possible to evaluate the absolute H-atom densities. The H-atom density, measured in the present vacuum system, was 1×10^{13} cm^{-3} when the H_2 pressure was 17 Pa and the

temperature of the W wire (30 cm in length and 0.38 mm in diameter) was 2200 K.[7,12] Then, the [H]/[H_2] population ratio should be 3×10^{-3}. The total pressure of the system has been observed to depend little on the wire temperature and the H_2 pressure should be independent of the wire temperature. The gas temperature should be ≈350 K, judging from the rotational temperature of OH, NH, and PH measured under similar conditions.[7,8,22,23] We have also shown that [H] increases in proportion to $[H_2]^{1/2}$ below 8 Pa,[2] while Comerford et al. have shown that [H] saturates over 1 kPa.[5] If we assume that the proportionality between [H] and $[H_2]^{1/2}$ is applicable up to 1 kPa and then saturates, the [H]/[H_2] ratio at 5.3 kPa is estimated to be 7×10^{-5}. This value is too small compared to the expected values when KR/D=10 or 1. The population ratio may depend on the distance from the wire, but the position of detection was near the middle point between the wire and the wall. It should be noted that the gradient in temperature compensates the diffusional loss.[24] We may conclude that the KR/D value in the present system must be less than 0.1 in the presence of more than 1 kPa of H_2.

Figure 4 illustrates the spatially integrated H-atom density divided by the wire surface area as a function of the wire radius for various values of KR/D. The integrated density increases drastically with the decrease in radius when KR/D is large, but this is not the case for small values of KR/D. The present calculations show that when KR/D=20, the integrated H-atom density increases by a factor of 3.5 when the wire radius, r_0, decreases from $0.05R$ to $0.001R$. However, when KR/D=0.1, the increase is less than 10%. In the present model, recombination processes of H atoms are not included, but this may not be a serious problem. The three-body recombination processes in the gas phase are minor under the present conditions.[25] The recombination processes on the chamber walls are implicitly included by the boundary condition that $C_A(r=R)=0$. The recombination on wire surfaces may also be minor since the surface area is much smaller than that of chamber walls.

Jansen et al. have presented a physical image of their results. They proposed that translationally hot H atoms produced near the wire surfaces may recoil the H_2 molecules approaching the wire when the mean-free-path is smaller than the wire diameter and that this effect is larger when a thinner wire is used. This may be true only when the

[H]/[H_2] ratio is large. At low H_2 pressures, the [H]/[H_2] ratio may be large, but under such conditions, the collisions between H and H_2 may become rare.

Finally, what was the problem in Jansen's experiments? They mention nothing about the chamber diameter. If they used a very thin cylinder, such as 1 cm in diameter, the wall temperature may have become very high and H atoms may have been produced efficiently in the gas phase. If this is the case, we have to mention that their chamber geometry is far from those for typical chemical vapor deposition processes. Another possibility is in the wire temperature measurements. In general, it is difficult to measure the wire temperature with a thermometer when the wire is thin. The activation energy for the production of H atoms calculated from Fig. 3 of Ref. 1, 100 kJ mol^{-1}, is much smaller than that reported by Redman et al. for Re, 230 kJ mol^{-1}.[6,26] A systematic error may have been present in the estimation of the wire temperature.

4. Conclusions

Two-photon laser-induced fluorescence measurements show that the density of H atoms produced from H_2 on heated W wire surfaces depends little on the wire diameter when the wire surface area and the temperature are kept constant. This result is supported by mathmatical modeling calculations. The modeling calculations of Jansen et al., suggesting the dependence of the H-atom densities normalized per unit surface area on the wire diameter, can only be applicable when the decomposition efficiency of H_2 is unreasonably high. Under typical decomposition conditions, only minor dependence is expected.

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Figure Captions

Fig. 1. (Color online) Catalyst temperature dependence of the electric power consumed in the presence of H_2 (circles), D_2 (triangles), and He (squares). Results in vacuum are represented by diamonds. The wire lengths and diameters were 40 cm and 0.3 mm (open symbols) or 30 cm and 0.4 mm (closed symbols), respectively. Gas pressures were 5.3 kPa.

Fig. 2. (Color online) Dependence of the H-atom density per unit surface area on the catalyst temperature, T_{cat}. The H_2 pressure was 5.3 kPa. The W wire diameters were 0.2 mm (open circle), 0.3 mm (closed circle), 0.4 mm (triangle), and 0.6 mm (square).

Fig. 3. (Color online) Calculated molecular (solid lines) and atomic (dashed lines) hydrogen densities, C_M and C_A, normalized by the H_2 density at the chamber walls, C_0, along the radial direction, r. The wire radius, r_0, and the decay length of decomposition, α, were both assumed to be $0.01R$, where R is the cylinder radius. D and K represent the diffusion coefficient and the integral of the reaction rate constant defined by Eq. (4).

Fig. 4. (Color online) Spatially integrated H-atom density divided by the wire surface area, in relative units, plotted as a function of the wire radius, r_0. The decay length, α, is $0.01R$, and the decomposition parameters, KR/D, are 20, 10, 1, and 0.1 from top to bottom. R, D, and K represent the cylinder radius, diffusion coefficient, and the integral of the reaction rate constant defined by Eq. (4).

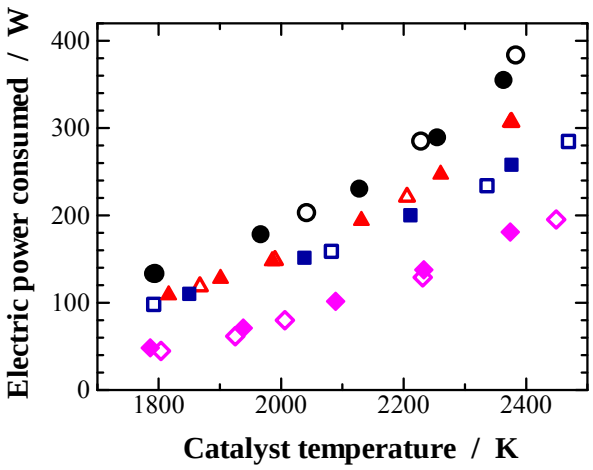
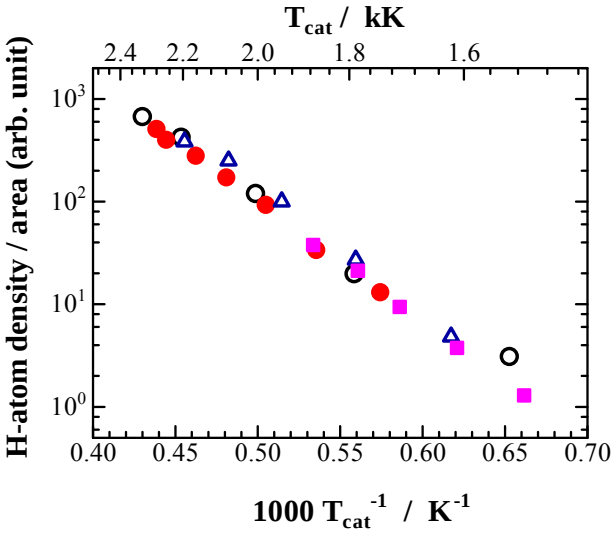

Electric power consumed / W
400
300
200
100
0
1800
2000
2200
2400
Catalyst temperature / K

Fig. 1


T_cat / kK
2.4
2.2
2.0
1.8
1.6
H-atom density / area (arb. unit)
10^3
10^2
10^1
10^0
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0.45
0.50
0.55
0.60
0.65
0.70
1000 T_cat^-1 / K^-1

Fig. 2

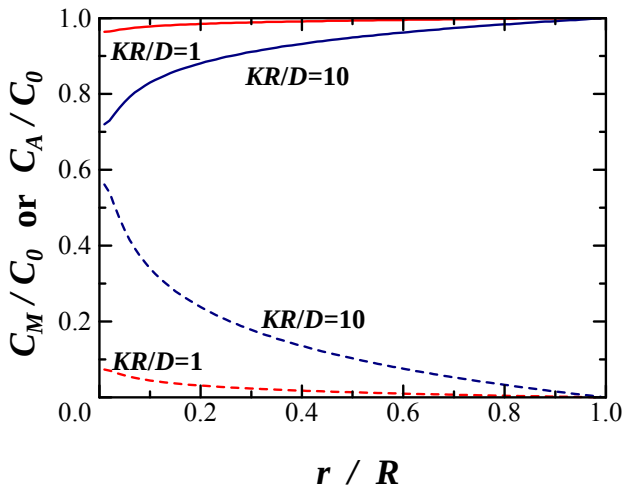
1.0
0.8
0.6
0.4
0.2
0.0
0.2
0.4
0.6
0.8
1.0
KR/D=1
KR/D=10
KR/D=10
KR/D=1
C_M / C_0 or C_A / C_0
r / R

Fig. 3

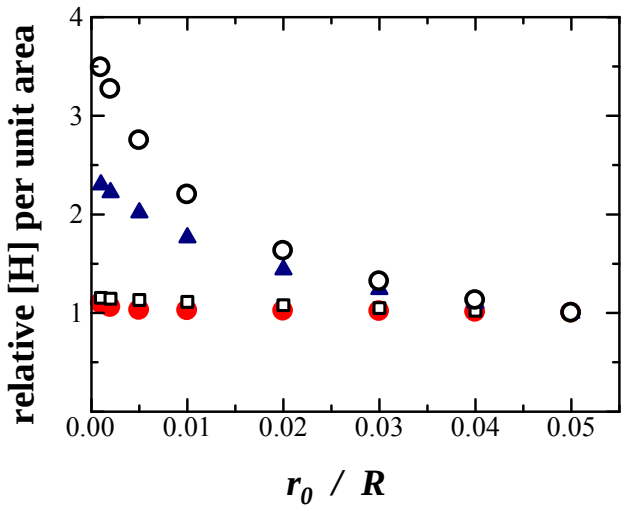

Fig. 4