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Dependence of the catalytic decomposition of PH₃ on wire material

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Abstract

The decomposition processes of PH₃ on heated W, Mo, Ta, and Ir surfaces were studied using mass spectrometric and laser spectroscopic techniques. For all wire materials, the decomposition efficiency saturated to around 50% at high wire temperatures. The P-atom density also saturated showing only minor dependence on the wire materials. At lower temperatures, however, the production rate of P atoms on Ta was higher than that on W, while that for Mo was lower, suggesting that the decomposition processes are not thermal but catalytic. The production rate on Ir was similar to that on W. Possible decomposition mechanisms are discussed.

Keyword

Catalytic decomposition, PH₃, Laser spectroscopy, Mass spectrometry

1. Introduction

Recently, we have studied the decomposition processes of PH_3 on heated W wire surfaces, employing both mass spectrometric and laser spectroscopic techniques [1]. Mass spectrometric measurements showed that PH_3 can be decomposed efficiently when the wire temperature is higher than 2000 K. From the absolute density measurements of H, P, PH, and PH_2 radicals, as well as their PH_3 flow rate dependences, we concluded that the major products on the wire surfaces are P and H atoms. The direct production processes of PH and PH_2 are minor and these radicals are produced in secondary reaction processes with H atoms, such as $\text{PH}_3 + \text{H} \rightarrow \text{PH}_2 + \text{H}_2$, in the gas phase. The P-atom density increases with wire temperature but tends to saturate at high temperatures. In other words, the temperature dependence is non-Arrhenius. These results are similar to those observed in the catalytic decomposition of SiH_4 , where the major products are Si and H atoms and the Si-atom density saturates at high temperatures [2-6]. In the decomposition of SiH_4 , decomposition efficiency depends on the wire materials [7]. It will be informative if a similar material dependence can be observed in the decomposition of PH_3 . Since the bond energy of H-PH₂ is only 332 kJ mol⁻¹, which is much weaker than that of H-NH₂ and H-SiH₃, PH_3 decomposition may be thermal rather than catalytic. If it is thermal, no wire-material dependence is expected.

In the present study, P-atom densities were measured as a function of wire temperature for four materials. Mass spectrometric studies to determine the decomposition efficiencies were also carried out. Wire-length and wire-diameter dependences were also examined for W.

2. Experimental Details

The experimental procedure and apparatus were similar to those described elsewhere [1]. PH_3 diluted with He to 2.0% was decomposed on a resistively heated wire installed in a cylindrical chamber evacuated by a turbomolecular pump (Osaka Vacuum, TG220FCAB). The internal diameter of the chamber was 10 cm, except where specified otherwise. The gas flow rate of PH_3/He was controlled by a mass flow controller (Horiba STEC, SEC-40M). The typical flow rate was 10 or 20 sccm (1 sccm = $6.9 \times 10^{-7} \text{ mol s}^{-1}$), while the total pressure was 2.0 or 3.5 Pa. H_2 was not introduced in any case. The wire temperature was evaluated from its electrical resistivity [8,9]. The wire diameters were 0.29, 0.39, or 0.49 mm for W, 0.39 mm for Mo and Ta, and 0.50 mm for Ir. The wire length was 30 cm unless otherwise stated. Two wires could be installed in the chamber and it was possible to measure not only the wire-temperature dependence but also the wire-material, wire-diameter, and wire-length dependences without breaking the vacuum.

Mass spectrometric analyses were carried out to measure the PH_3 and H_2 densities. A quadrupole mass-spectrometer (Anelva, M-QA200TS) was attached to the chamber through a sampling hole. The flight tube was differentially pumped down to 5×10^{-4} Pa with another turbo molecular pump (Osaka Vacuum, TG350FCWB). The absolute densities of H_2 were evaluated by comparing the H_2^+ mass signal with that when a known amount of H_2/He was flown.

A vacuum-ultraviolet (VUV) laser-induced fluorescence (LIF) technique was employed to detect P atoms. A four-wave mixing technique was used to produce laser pulses at 177.5 nm, which correspond to the $3s^23p^24s \ ^4P_{5/2} - 3s^23p^3 \ ^4S_{3/2}$ resonance transition of P atoms. Xe was used as a nonlinear optical medium to produce VUV

radiation. The induced fluorescence was detected with a solar-blind photomultiplier tube (Hamamatsu Photonics, R6835) through an MgF₂ collimating lens and an interference filter (Acton Research, 180-N). The absolute densities of P atoms were estimated from the imprisonment lifetime of P(3s²3p²4s ⁴P_{5/2}) at a wire temperature of 2400 K and total pressure of 100 Pa.

PH₃ (Japan Air Gases, diluted with He to 2.0%) and Xe (Teisan, 99.995%) were used from cylinders without further purification. W (99.95%), Mo (99.95%), and Ta (99.95%) wires were products of Nilaco, while the product of Tanaka Precious Metals was used for Ir (99.9%).

3. Results

Fig. 1 shows the dependence of the mass signals of PH₃ and H₂ on wire temperature for W, Mo, and Ta. The flow rate of PH₃/He and the total pressure were 20 sccm and 3.5 Pa, respectively. It is clear that PH₃ is consumed efficiently at temperatures above 1500 K, but the mass signals for PH₃ level off over 2000 K. The results for H₂ are complementary. Similar wire-temperature dependences were observed for Ir and the wire-material dependence was not remarkable. As for W, the wire diameter was changed between 0.29 and 0.49 mm, while the wire length was changed between 20 and 40 cm. Table 1 summarizes the decomposition efficiencies of PH₃ at 2200 K under various conditions. Decomposition efficiency increases slightly with increases in wire length and diameter and decreases with flow rate, although the changes are not drastic. The chamber-size dependence was not remarkable, either.

The P-atom densities were also measured as a function of wire temperature. Fig. 2 illustrates the Arrhenius plots for W, Mo, and Ta. The flow rate and the total pressure

were 10 sccm and 2.0 Pa, respectively. Similar results were obtained for Ir and the plots were nonlinear in all cases. The limiting values of P-atom densities at high temperatures were almost the same, but the slopes at low temperatures were different. Although the density on Ir is similar to that on W, at low temperatures, the density on Ta is higher than that on W, while that on Mo is lower. P-atom density increased with an increase in the length of the W wire at all temperatures, as shown in Fig. 3.

4. Discussion

The fact that the limiting values of the P-atom densities agree at high wire temperatures suggests that P and H atoms are the only major products not only for W, but also for other wire materials, and that the direct production processes of PH and PH₂ radicals are minor. In other words, P-atom density can be a measure of the decomposition rate of PH₃. As has been mentioned, the production rate of P atoms depends on the wire material at low temperatures, but the difference in decomposition efficiencies is not clear in mass spectrometric measurements. The final product analysis, such as the present mass spectrometric study, must be less sensitive when the decomposition efficiency saturates.

The dependence of P-atom densities on the wire material at low temperatures shows that the decomposition processes are not thermal but catalytic in nature. A similar tendency has been observed in the decomposition of SiH₄ [6,7], but in that case the decomposition mechanism may be different. In the catalytic decomposition of SiH₄, the apparent activation energies for Ta and Mo were larger than those for W and Re and close to the corresponding Si thermal desorption energies [7]. Duan and Bent considered that the decomposition of SiH₄ on Ta and Mo is controlled by the desorption

processes from the bare metal surfaces. For W and Re, on the other hand, they proposed that Si layers are formed on the metal surfaces and the activation energies represent those for Si-atom desorption from these layers. In the present PH₃ system, the activation energies for W and Mo are not greatly different, although that for Ta is a little smaller and that for Ir is a little larger. The similarity between W and Mo might suggest that the wire surfaces are completely covered with P layers. However, this is less likely judging from the difference in the production efficiencies of P atoms on these metal surfaces at low temperatures. In addition, the vapor pressure of phosphorus must be too high. W is easily silicided when exposed to SiH₄ at low temperatures. On the other hand, the phosphorization of W seems to be minor, judging from the absence of aging changes in electric resistivity and catalytic activity when a W wire was exposed to PH₃ under heated conditions. The similarity in the activation energies for W and Mo may represent similar desorption energies of P atoms from these metal surfaces.

The minor temperature dependence of PH₃ and P-atom densities at high temperatures can be explained, at least qualitatively, by the following simple mechanism:

The rate constants are represented by k_i , while PH₃(ad) stands for adsorbed PH₃. This mechanism is basically the same as that proposed by Duan and Bent for the decomposition of SiH₄ [7] and the spatial non-uniformity of gas temperature and radical

densities are not taken into account just for simplicity. The production processes of PH and PH₂ are not included, either. The process to produce P+3H is not an elementary reaction but a complex one, which should be divided into several steps, but the detailed steps were not presented. Under steady-state conditions, the densities of PH₃ and P, [PH₃] and [P], should be given by:

$$[\text{PH}_3] = \frac{k_{in}(k_{-1} + k_2)}{k_1k_2 + k_{out}(k_{-1} + k_2)},$$

$$[\text{P}] = \frac{k_1k_2}{k_3} \frac{k_{in}}{k_1k_2 + k_{out}(k_{-1} + k_2)}.$$

The decomposition efficiency, ϕ , is given by:

$$\phi = 1 - \frac{k_{in}(k_{-1} + k_2)}{k_1k_2 + k_{out}(k_{-1} + k_2)} \frac{k_{out}}{k_{in}} = \frac{k_1k_2}{k_1k_2 + k_{out}(k_{-1} + k_2)}$$

The rate constants other than k_{-1} and k_2 may be temperature independent. Since the production of P+3H from PH₃ is endothermic, the activation energy for k_2 must be larger than that for k_{-1} . Then, k_2 may be much smaller than k_{-1} at low temperatures. Under such conditions,

$$\phi = \frac{k_1k_2}{k_1k_2 + k_{out}k_{-1}},$$

$$[\text{P}] = \frac{k_1k_2}{k_3} \frac{k_{in}}{k_1k_2 + k_{out}k_{-1}},$$

and these values are temperature dependent. On the other hand, if the pre-exponential factor for k_2 is much larger than that for k_{-1} , k_2 may be larger than k_{-1} at high temperatures, and the temperature independence can be derived:

$$\phi = \frac{k_1}{k_1 + k_{out}},$$

$$[\text{P}] = \frac{k_1}{k_3} \frac{k_{in}}{k_1 + k_{out}}.$$

The nonlinear increase in the decomposition efficiency at 2200 K with the wire length/diameter, shown in Table 1, can also be explained with this model if k_1 is proportional to the surface area of the wire.

Although the above model can give us a qualitative explanation of present results, it is too simple to account for them quantitatively. For example, ϕ saturates over 2000 K, while [P] starts to saturate at 2400 K. According to the above model, [P] must be proportional to ϕ at all temperatures. For quantitative discussion, more sophisticated modeling studies are desired.

5. Conclusion

PH₃ can easily be decomposed on heated W, Mo, Ta, and Ir surfaces to produce P atoms. At lower temperatures, the production rate of P atoms on Ta is higher than the rate on W, while that for Mo is lower, suggesting that the decomposition processes are not thermal but catalytic. At high temperatures, on the other hand, the P-atom production rate saturates and the saturated density shows only a minor dependence on wire material. Both decomposition efficiency and P-atom density increase with the wire size. These results can be explained qualitatively by a simple model which includes the desorption processes of physisorbed PH₃ from the catalyst.

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Table and Figure Captions

Table 1 Decomposition efficiency of PH_3 at 2200 K^a

Fig. 1. Dependence of PH_3 and H_2 densities on the wire temperature. Wire materials were W (square), Mo (circle), and Ta (triangle). Open symbols represent the results for PH_3 , while closed symbols represent those for H_2 . The wire length and diameter were 30 cm and 0.39 mm, respectively. The flow rate and the total pressure of PH_3/He were 20 sccm and 3.5 Pa, respectively.

Fig. 2. Wire temperature dependence of P-atom densities. Wire materials were W (square), Mo (circle), and Ta (triangle). The wire length and diameter were 30 cm and 0.39 mm, respectively. The flow rate and the total pressure of PH_3/He were 10 sccm and 2.0 Pa, respectively.

Fig. 3. W-wire temperature dependence of P-atom densities. The wire diameter was 0.39 mm, while the lengths were 20 cm (diamond), 30 cm (square), and 40 cm (circle). The flow rate and the total pressure of PH_3/He were 10 sccm and 2.0 Pa, respectively.

Table 1

Decomposition efficiency of PH_3 at 2200 K^a

Wire material	Length /cm	Diameter / mm	PH_3 flow rate / sccm	Decomposition efficiency
W	20	0.39	20	0.43
W	30	0.39	20	0.49
W	40	0.39	20	0.51
W	30	0.29	20	0.44
W	30	0.49	20	0.51
W	30	0.39	10	0.56
W	30	0.39	30	0.43
W ^b	30	0.39	20	0.45
W ^b	30	0.39	10	0.53
W ^b	30	0.39	30	0.40
Mo	30	0.39	20	0.51
Ta	30	0.39	20	0.43
Ir	30	0.50	20	0.51

a: The internal diameter of the chamber was 10 cm otherwise stated.

b: The internal diameter of the chamber was 28 cm.

Fig. 1.

Fig. 2.

Fig. 3