TPD Study on the Decomposition Mechanism of 2,2,6,6-tetramethyl-3,5-heptadione on Pt foil

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Among techniques for the preparation of metal oxide film, metal organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) are preferred for their advantages [1, 2]. However, process parameters for them are strongly restricted by the properties of precursors [2, 3].

Even though the knowledge of the kinetics or the reaction mechanism of precursors on the substrate surface is essential to the selection of the optimum process condition that yields the best film quality, little work has been done to clarify the adsorption mechanism and the surface chemistry of the precursor at a fundamental level.

The present work aims at understanding how 2,2,6,6-tetramethyl-3,5-heptadione (TMHD), which is generally used for ligand in metal beta-diketonate, adsorbs and decomposes on the Pt surface at various temperatures. It is important to know the behavior of TMHD on Pt because carbon impurities are produced as residues of this organic compound. We have investigated the adsorption of TMHD on Pt foil at 150K, and its decomposition and desorption behavior during annealing by temperature programmed desorption (TPD) technique in vacuum. TPD spectra were taken after the surface was exposed to TMHD dosed in the amounts ranging from 0.8L to 12L.

Fig. 1 shows the desorption spectra of m/e=2, 16, 29, 41, 43, and 45 signals at the dosage of 1.3L TMHD representing hydrogen, methane, acetaldehyde, propylene, iso-propanol, and propylene, respectively. All cracking fragments observed at each desorption state and possible structures of desorbed molecules are listed in Table 1.

The desorption peaks at 200K represent the desorption of molecularly adsorbed TMHD since intensity ratios of other fragmentation species are similar to those obtained for gaseous TMHD [4].

The peaks of hydrogen are observed at 250K and 440K, result from the desorption of molecularly or atomically adsorbed hydrogen on Pt [5]. Surface hydrogen on Pt is produced by the decomposition of t-butyl species in TMHD [6].

Desorption peak of m/e=16 is observed at 400K, which could be assigned to methane, produced by the decomposition of t-butyl in TMHD. Accordingly, t-butyl in TMHD is easily decomposed at low temperatures [7].

The desorption peaks of m/e=29 and 45, representing acetaldehyde and iso-proanol, respectively, are also observed at 400K, which are produced by C-C bond breaking in TMHD.

At 500K, desorption peaks of m/e= 41, 29, and 43, representing propylene, acetaldehyde, and acetone, respectively, are observed. Propylene may come from the decomposition of t-butyl in TMHD and acetaldehyde and acetone result from the decomposition of TMHD backbone.

In summary, surface reactions that proceed at different surface temperatures may be schematically presented as in Fig. 2.

References

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Table 1. The major cracking fragments observed at each desorption state and the tentative structures of desorbing species in the desorption of TMHD from Pt foil.

Desorption state(K)	Cracking fragments	Tentative species
200K		TMHD
250K	**2**, 1	H_2
400K	**16**	CH4
	29, 44, 15	CH_3CHO
	45, 43, 27	$CH_3CHOHCH_3$
440K	**2**, 1	H_2
500K	**41**, 42	CH_2CHCH_3
	29, 44,15	CH_3CHO
	43, 58	CH_3COCH_3

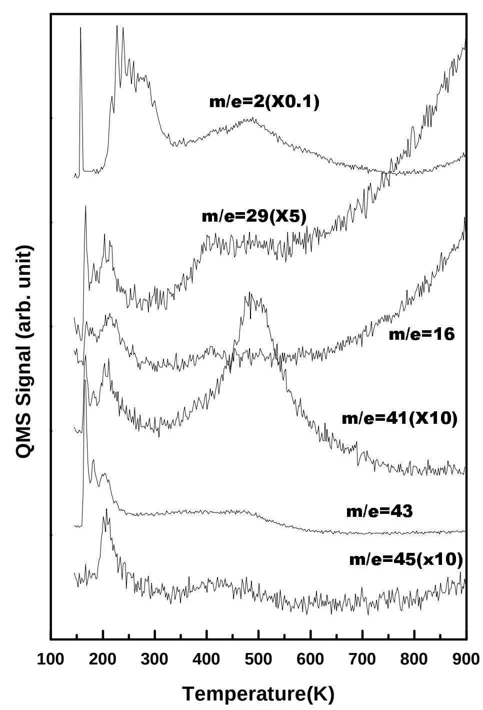

Figure 1. Thermal desorption spectra obtained on Pt foil exposed to 1.3L of TMHD at 150K and at a heating rate of 0.5K/s.

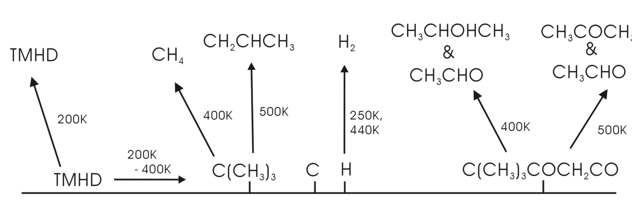

Figure 2. Schematic diagram of the proposed decomposition and reaction mechanism of TMHD on Pt surface.