

## Adsorption of Water Vapor on Crystalline Phases of V-P-O

Yusaku TAKITA,\* Tomoya SAKAI, Yukako MIZUHARA, and Tatsumi ISHIHARA  
Department of Environmental Chemistry and Engineering,  
Faculty of Engineering, Oita University, Oita 870-11

Adsorption of water vapor on crystalline compounds of V-P-O was examined by a TPD method. Water molecules chemisorbed on the V-P-O compounds composed of V(IV) ions such as  $\alpha$ - and  $\beta$ -(VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and VO(PO<sub>3</sub>)<sub>2</sub>, were desorbed at 400 °C. However, from compounds consisting of V(V) like V<sub>2</sub>O<sub>5</sub> and VOPO<sub>4</sub>, only physically adsorbed water molecules were desorbed at 80-200 °C. It can be concluded that the valence of V ions is a key factor for the chemisorption of water vapor on V-P-O compounds.

(VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> was thought to be an active phase for the oxidation of butane into maleic anhydride (MA). It has been known that the addition of water vapor strongly affects the butane oxidation over the (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> catalyst. For example, the addition of 10 mol% water vapor brings about a decrease in the conversion of butane by about 13% and an increase in the MA selectivity by about 10% when oxidized at 450 °C. Arnold and Sundaresan<sup>1)</sup> proposed the following explanation for the effect. Adsorbed water molecules withdraw phosphate ions from bulk to the surface and the resulting concentrated surface phosphate ions affect the catalysis. However, no experimental evidence was reported. Therefore, the mechanism of this promotion effect remains obscure. Some information concerning the adsorption of water vapor onto the crystalline phases of V-P-O is helpful for understanding the origin of the effect.

The authors have found out that the valence of vanadium ions plays a key role in the adsorption of water vapor onto the crystalline phases of V-P-O. This fact will be discussed in this paper.

V-P-O compounds were prepared by ordinary preparation methods using V<sub>2</sub>O<sub>5</sub>, NH<sub>2</sub>OH·HCl, phosphoric acid in an aqueous and isobutanol medium. Detailed preparation procedures appeared elsewhere.<sup>2-4)</sup> H<sub>3</sub>PO<sub>4</sub> was supported onto (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> using the filled pore method. The surface area of the samples were 5.9, 18.2, 18.6, 12.9, and 3.2 m<sup>2</sup>/g for V<sub>2</sub>O<sub>5</sub>,  $\alpha$ -(VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>,  $\beta$ -

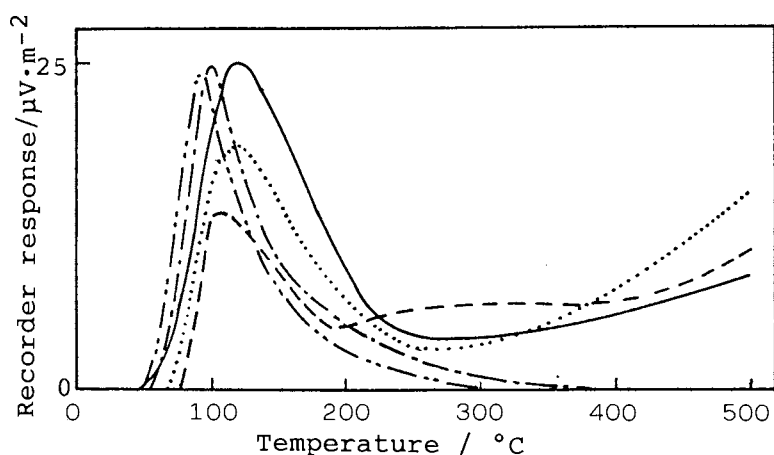


Fig. 1. TPD spectra of water vapor from V-P-O compounds.

---  $V_2O_5$ ,      - · - · -  $VOPO_4$   
 .....  $VO(PO_3)_2$ ,      —  $\alpha-(VO)_2P_2O_7$   
 .....  $\beta-(VO)_2P_2O_7$

$(VO)_2P_2O_7$ ,  $VOPO_4$ , and  $VO(PO_3)_2$ , respectively. Samples were evacuated at 500 °C for 1 h and then the mixture of water vapor and He was circulated onto the sample at 500 °C for 30 min and the temperature was decreased to room temperature at a rate of 10 °C/min. Temperature Programmed Desorption (TPD) measurement was carried out in a He flow (30 cm<sup>3</sup>/min) and at a rate of 10 °C/min.

TPD spectra of water vapor adsorbed on some V-P-O compounds are shown in Fig. 1. TPD spectrum from  $V_2O_5$  consisted of a sole peak with a peak top at about 90 °C and no desorption of water vapor was detected at temperatures higher than 300 °C. This peak can be ascribed to the desorption of water vapor physically adsorbed on V(V) ions.  $VOPO_4$ , which is composed of V(V), gave a TPD spectrum quite similar in shape to that of  $V_2O_5$ .

There are three modifications of  $(VO)_2P_2O_7$ , i.e.,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -type.  $\alpha-(VO)_2P_2O_7$  gives X-ray diffraction peaks due to (020) plane much more intense than that of (204) plane and  $\beta-(VO)_2P_2O_7$  gives peaks with converse intensity.  $\gamma-(VO)_2P_2O_7$  gives both peaks with comparable intensity.

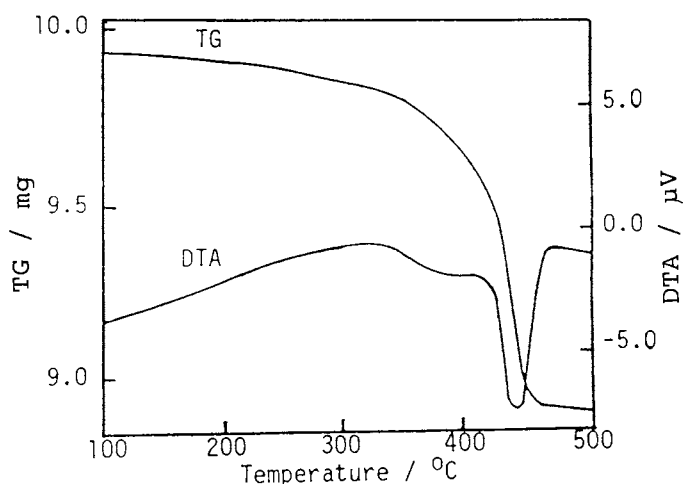


Fig. 2. TG-DTA curves of  $H_4(VO)_2P_2O_9$ .  
 $N_2$ : 150 cm<sup>3</sup>·min<sup>-1</sup>, 10 °C·min<sup>-1</sup>.

As can be seen from Fig. 1, desorption of water vapor took a maximum at around 120 °C and then increased from 250 °C to 500 °C in the cases of  $\alpha$ - and  $\beta$ - $(VO)_2P_2O_7$  which were composed of V(IV).

$VO(PO_3)_2$  is also composed of V(IV). Desorption spectrum of water vapor of  $VO(PO_3)_2$  appeared to consist of three desorption peaks at 50-200 °C, 200-400 °C, and >400 °C.

Table 1. Desorption of water vapor from various V-P-O catalysts

Sample	Specific surface area (m <sup>2</sup> /g)	Desorbed amount of water vapor (μmol/m <sup>2</sup> ) <sup>a)</sup>	
		total	>250 °C
V <sub>2</sub> O <sub>5</sub>	5.9	3.06	0
VO(PO <sub>3</sub> ) <sub>2</sub>	3.2	2.85	1.94 (>190 °C)
α-(VO) <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	18.2	2.30	0.80
β-(VO) <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	18.6	2.08	1.04
VOPO <sub>4</sub>	12.9	1.66	0

a) Calculated from Fig.1.

Amounts of water vapor desorbed from the samples are listed in Table 1. 43 μmol/m<sup>2</sup> of water is required to accomplish monolayer coverage over (020) plane of (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, assuming that a water molecule is adsorbed on a couple of surface VO<sub>6</sub> units as depicted in Fig.4. Similar amounts of water will be required for monolayer coverage over the other compounds. The observed amounts are much smaller than that of monolayer coverage. Therefore, the detected peaks in TPD chromatograms can be ascribed to the water molecules adsorbed on the samples.

The results of TG-DTA analysis of H<sub>4</sub>(VO)<sub>2</sub>P<sub>2</sub>O<sub>9</sub> are also shown in Fig.2 as a reference. H<sub>4</sub>(VO)<sub>2</sub>P<sub>2</sub>O<sub>9</sub> has the structure in which a water molecule coordinates with a PO<sub>4</sub> unit and another water molecule coordinates with a VO<sub>6</sub> unit of (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. It can be seen from the TG-DTA data that the water molecules coordinating with both units are desorbed at >200 °C.

The TPD spectra of water vapor from the (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> on which phosphoric acid was supported are shown in Fig.3. In these samples, the

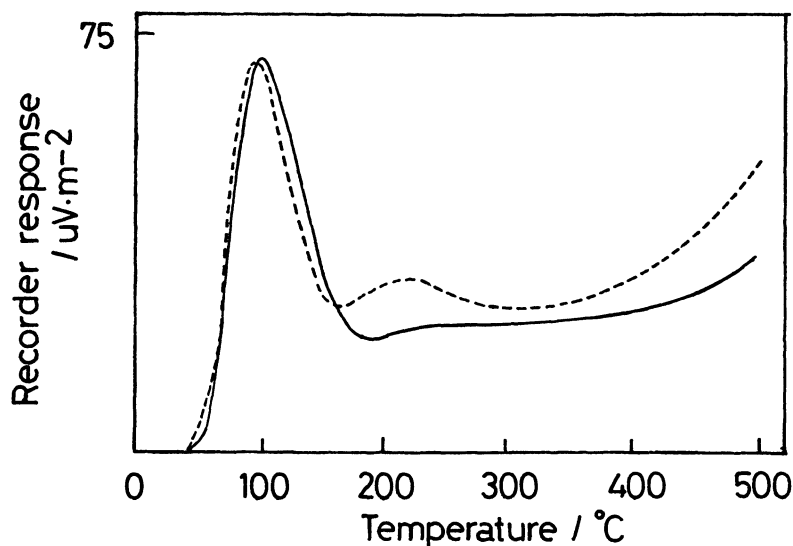


Fig.3. TPD spectra of water vapor from (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> with supported H<sub>3</sub>PO<sub>4</sub>.

— 7.95 wt%  
 ---- 23.9 wt%  
 (as P<sub>2</sub>O<sub>5</sub>)

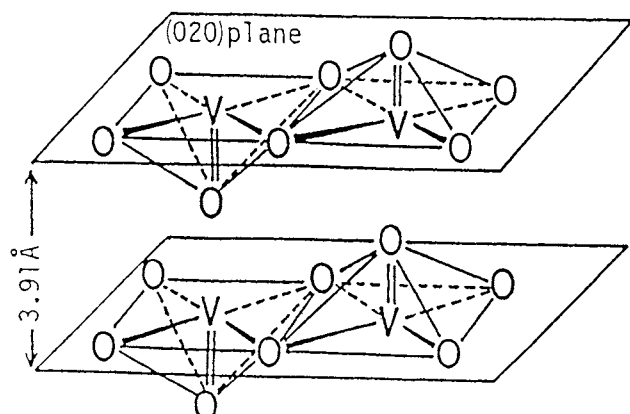


Fig.4. Arrangement of  $\text{VO}_6$  units.

desorption of water vapor at 200-500 °C increased and especially at 200-350 °C. This suggests that the water molecules adsorbed on phosphate ions are desorbed at a wide temperature range of 200-500 °C.  $\text{VO}(\text{PO}_3)_2$  is a sole compound having P/V ratio higher than unity among the compounds examined. In the TPD spectrum from this compound, we can see a relatively large desorption peak at 200-400 °C. This may reflect the adsorption of water vapor on phosphate ions.  $\text{V}_2\text{O}_5$  gives no desorption of chemisorbed water vapor. However, the  $\text{V}_2\text{O}_5$  deeply reduced by hydrogen, gave the desorption at temperatures higher than 400 °C. This suggests that the desorption at 400 °C is due to chemisorbed water vapor on V(IV). The structure of the compounds, i.e. the arrangement of  $\text{VO}_6$  and  $\text{PO}_4$  units, is a rather minor factor because  $\text{V}_2\text{O}_5$  and  $(\text{VO})_2\text{P}_2\text{O}_7$  possess the same structure as depicted in Fig.4. If water molecules are adsorbed by their nucleophilic interaction with the surface adsorption sites, V(V) ions should be more favorable than V(IV) ions for the adsorption of water vapor in contrast to the experimental results. Although the reason is not clear at this stage, it is evident that water molecules can adsorb only on V(IV) ions of V-P-O compounds. Perhaps, the information concerning the detailed surface structure of these V-P-O compounds may account for the experimental results.

This work was partly supported by a Grant-in-Aid #03650682 (1991) for Scientific Research from Ministry of Education, Science, and Culture of Japan.

#### References

- 1) E. Arnold and S. Sundaresan, *Appl. Catal.*, **41**, 225(1988).
- 2) Y. Takita, K. Tanaka, S. Ichimaru, and T. Ishihara, *J. Catal.*, **130**, 347 (1991).
- 3) Y. Takita, *Hyomen*, **27**, 534(1989).
- 4) E. Bordes and P. Courtine, *J. Catal.*, **57**, 236(1979).

(Received November 11, 1991)