The Role of Brønsted and Lewis Acid Sites of Vanadyl Pyrophosphate Measured by Dimethylpyridine-temperature Programmed Desorption in the Selective Oxidation of Butane

Yuichi KAMIYA T),*1, Hiroyuki NISHIYAMA T), Miki YASHIRO T), Atsushi SATSUMA T), and Tadashi HATTORI T)2

T)1) Research and Development Center, Tonen Chemical Corp., 3-1 Chidori-cho, Kawasaki-ku, Kawasaki 210-0865, JAPAN
T)2) Dept. of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, JAPAN

(Received August 8, 2002)

Acidic properties of three types of (VO)2P2O7 catalysts were investigated by temperature programmed desorption (TPD) using 3,5- and 2,6-dimethylpyridine as probes, and the selective oxidation of butane to maleic anhydride (MA) was performed. VPO-org was prepared in organic solvent, VPO-redu was obtained by reduction of VOPO4·2H2O, and VPO-aq was prepared in aqueous medium. 3,5-Dimethylpyridine (3,5-DMP) is adsorbed on both Brønsted and Lewis acid sites, whereas 2,6-dimethylpyridine (2,6-DMP) is selectively adsorbed on Brønsted acid sites due to the steric hindrance of the two methyl groups, so the amounts and strengths of the Brønsted and Lewis acid sites could be determined separately. The (VO)2P2O7 catalysts had four types of acid sites: weak and strong Brønsted acid sites, and weak and strong Lewis acid sites. The acidic properties were greatly dependent on the preparation methods as follows: VPO-org had a larger amount of the strong Brønsted acid sites and these acid sites were relatively weak. VPO-redu had a larger amount of the strong Lewis acid sites and VPO-aq had fewer acid sites. The selectivity to MA at low conversion increased with the amount of strong Lewis acid sites, indicating that the strong Lewis acid sites are important for MA formation. The strong Brønsted acid sites may promote the consecutive oxidation of MA.

Keywords
Vanadyl pyrophosphate catalyst, Acidic property, Dimethylpyridine, Temperature programmed desorption, Butane oxidation, Maleic anhydride

1. Introduction

Vanadyl pyrophosphate, (VO)2P2O7, demonstrates a characteristic activity for the selective oxidation of butane to maleic anhydride (MA), and is used as the main component of industrial catalysts for this reaction1 4). The catalytic performance of this catalyst greatly depends on the preparation method and conditions5,13). Although many investigations have focused on this reaction system, the nature of the active sites on the (VO)2P2O7 catalyst is still controversial.

Both redox sites and acid sites may be significantly involved in the selective oxidation of paraffins over solid catalysts5). In addition, Brønsted and Lewis acid sites have different functions in selective oxidation, and the strength of these respective acid sites strongly affects the catalytic performance6). Investigation of the involvement and function of acid sites on (VO)2P2O7 catalysts in the selective oxidation of butane has shown that the acid sites are necessary for this reaction, since adding ammonia to the reaction feed and doping of potassium to the catalyst make the activity for MA formation lowered7). Both Brønsted and Lewis acids are present on (VO)2P2O7 based on the IR spectra of basic molecules adsorbed on the catalyst8). The ratio of Lewis to Brønsted acid sites has been estimated from the IR spectra of pyridine adsorbed on (VO)2P2O79). However, quantitative determinations of individual Brønsted and Lewis acid sites have not been performed.

Temperature-programmed desorption (TPD) of basic molecules is a useful method for the determination of acid amount as well as acid strength of solid catalysts10 13). Ammonia is used frequently as the probe molecule, but the amount and strength of the Brønsted and Lewis acid sites can not be estimated separately, because of the non-selective adsorption of ammonia. Benesi14) suggested that 2,6-dimethylpyridine (2,6-DMP) could be used as a probe to selectively detect the
protonic sites due to steric hindrance of the two methyl groups near the nitrogen atom. In contrast, 3,5-dimethylpyridine (3,5-DMP) is adsorbed on both Bronsted and Lewis acid sites non-selectively. Consequently, if both dimethylpyridines are used as probe molecules for TPD measurement, both the amount and strength of Bronsted and Lewis acid sites can be determined.

Our previous paper demonstrated that Bronsted and Lewis acid sites can be estimated separately by TPD of 2,6-DMP and 3,5-DMP by use of typical samples of solid acids, that is, alumina, alumina-boria and silica-magnesia. The present study examined the acidic properties of (VO)₂P₂O₇ catalysts by the DMP-TPD method. Further, the catalytic performance of three types of (VO)₂P₂O₇ catalysts were assessed for the selective oxidation of butane based on acidic properties.

2. Experimental

2.1 Preparation of Catalysts

Three types of (VO)₂P₂O₇ catalysts were prepared according to the literature. V₂O₅ (0.08 mol; Koso Chemical Co., Ltd.) was added to a mixture of 90 cm³ of isobutyl alcohol (Koso Chemical Co., Ltd.) and 60 cm³ of benzyl alcohol (Koso Chemical Co., Ltd.). This suspension was refluxed at 378 K for 3 h. The resulting yellow solid was filtered, washed with acetone and dried at room temperature for 16 h. The catalyst precursor then was treated at 823 K for 2 h in N₂ flow (300 cm³ min⁻¹). VPO-org was prepared in organic solvent. V₂O₅ (0.1 mol) was added to an aqueous solution (200 cm³) of NH₂OH·HCl. This mixture was again refluxed at 378 K for 3 h. The resulting light blue solid was filtered, washed with acetone and dried at room temperature for 16 h.

2.2 Characterization

X-Ray diffraction (XRD) patterns of the catalysts were measured by using an X-ray diffractometer (Rigaku RINT-1400) with Cu Ka radiation (λ = 0.154 nm). Scanning electron microscope (SEM) images of the catalysts were taken with a scanning electron microscope (HITACHI S-2100B). X-Ray photoelectron spectra (XPS) were obtained with a Physical Electronics Model 5600ci spectrometer with Mg Kα radiation. The surface P/V ratio was determined by multiplying the XPS peak intensity ([I(P)/I(V)]) by a correction factor (2.75). The P/V ratio of catalyst bulk was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES; Shimadzu ICPS-8000). The catalyst powder was dissolved into hot H₂SO₄, and the solution was diluted with water to about 30 ppm of V or P. The surface area of the catalyst was measured by a BET method using N₂ with a Carlo Erba Sorptomatic Model-1800 after the sample was stood under a vacuum at 473 K for 2 h.

2.3 Temperature Programmed Desorption of Dimethylpyridine (DMP-TPD)

DMP-TPD was performed using the same apparatus as reported previously. 2,6-DMP and 3,5-DMP were used as the probe molecules. A U-shaped tube made of quartz was used as the sample cell. The sample powder (100 mg) was placed in the sample cell and pretreated at 673 K for 2 h in a flow of dehydrated He at 150 cm³ min⁻¹. After cooling to 523 K under the He flow, the sample powder was exposed to a stream of the probe molecules diluted in He for 30 min. Equilibrium adsorption was confirmed by measurement of the concentration of probe molecules passed through the sample cell. The sample was kept at 523 K for 2 h in the He flow to purge excess or weakly adsorbed probe molecules. The temperature of the sample powder was then raised from 523 K to 1073 K at 5 K min⁻¹ in the He flow and the probe molecules desorbed from the sample were detected with a flame-ionization detector (FID, Shimadzu GC-9A). The line between the sample cell and the detector was heated at 400 K.

2.4 Catalytic Oxidation of Butane

Catalytic oxidation of butane was carried out in a flow reactor (Pyrex tube, inside diameter of 6 mm) under atmospheric pressure at 723 K. A mixture of 1.5 vol% butane, 20 vol% O₂ and N₂ (balance) at a total flow rate of 10 cm³ min⁻¹ was fed over the catalyst bed. The conversion of butane was controlled by the weight of the catalyst under the constant flow rate. The products were analyzed with on-line gas chromatographs.
(FID (Shimadzu 14A, Shimadzu 9A) and thermal conductivity detector (Shimadzu 9A)) equipped with a Porapak QS column (inside diameter 2.2 mm, length 1 m) for butane and MA, and a Porapak N column (inside diameter 2.2 mm, length 2 m) for CO₂. A Molecular Sieve 13X column (inside diameter 2.2 mm, length 4 m) was also used to separate O₂, N₂ and CO. CO and CO₂ were converted to methane by using a Methanizer (Shimadzu MTN-1) for more sensitive detection by the FID-GC. Prior to the analysis, the catalysts were aged in the reaction mixture at 723 K for 10 h.

3. Results and Discussion

3.1. Structure of the Catalysts

The XRD patterns of the catalysts are shown in Fig. 1. The positions of the diffraction lines for these catalysts were same as those of (VO)₂P₂O₇[^16] and no lines due to other phases such as VOPO₄ were observed. The relative intensities and the line-widths greatly differed depending on the catalysts. The (100) line of VPO-org was very weak and broad, indicating the presence of the structural disorder in the plane of layer stacking[^21], whereas the diffraction lines of the other two catalysts were strong and sharp as previously reported[^6].

The SEM images are shown in Fig. 2. The morphologies of VPO-org, VPO-redu, and VPO-aq were rose-like, plate-like and block-like, respectively, and consistent with those reported[^16].

The bulk and surface P/V ratios and the BET surface areas are summarized in Table 1. The bulk P/V ratios of the catalysts were close to 1. The surface P/V ratios of VPO-org and VPO-redu were 1.2, whereas that of VPO-aq was 1.5. The BET surface areas were determined to be 33.0, 24.0 and 5.4 m²g⁻¹ for VPO-org, VPO-redu and VPO-aq, respectively.

3.2. Acidic Property of the Catalysts

Figure 3 shows the TPD spectra of 2,6-DMP and 3,5-DMP, with the desorption rates expressed per unit surface area. The differential spectra calculated by subtracting the 2,6-DMP-TPD spectra from 3,5-DMP-TPD ones are also shown. As verified in our previous study[^15], 2,6-DMP is adsorbed on the Brønsted acid sites selectively with purging at 523 K for 2 h, unless very strong Lewis acid sites with exceptional behavior are present. 3,5-DMP is adsorbed on both Brønsted and Lewis acid sites. In the TPD spectrum of 3,5-DMP for silica-magnesia which has no very strong Lewis acid sites, desorption of 3,5-DMP continued up to 950 K[^15], but this desorption was scarcely observed over 900 K for the (VO)₂P₂O₇ catalysts. These results

![XRD Patterns of the Catalysts](image1.png)

![SEM Images of the Catalysts](image2.png)

![Table 1 Compositions and Surface Areas of (VO)₂P₂O₇ Catalysts](table1.csv)

**Table 1 Compositions and Surface Areas of (VO)₂P₂O₇ Catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>P/V ratio</th>
<th>Surface area [m²g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPO-org</td>
<td>1.04</td>
<td>33.0</td>
</tr>
<tr>
<td>VPO-redu</td>
<td>1.06</td>
<td>24.0</td>
</tr>
<tr>
<td>VPO-aq</td>
<td>1.07</td>
<td>5.4</td>
</tr>
</tbody>
</table>

a) Determined by ICP-AES.
b) Determined by XPS. These ratios were calculated as 2.75 × \( \frac{I(P)}{I(V)} \)^[^10].
indicate that the (VO)$_2$P$_2$O$_7$ catalysts do not have the very strong Lewis acid sites. The desorption temperatures of 2,6-DMP and 3,5-DMP adsorbed on one material are demonstrated to be almost the same, although the chemical properties, e.g., pK$_b$ and vaporization enthalpy, of these isomers are slightly different$^{15)}$. Therefore, 3,5-DMP-TPD, 2,6-DMP-TPD and the differential spectra indicate the total, Brønsted and Lewis acid sites, respectively. The spectra confirmed that the (VO)$_2$P$_2$O$_7$ catalysts have both Brønsted and Lewis acid sites$^{8)}$. The spectra of Brønsted and Lewis acid sites exhibited two desorption peaks, indicating the existence of at least four types of acid sites, that is, weak and strong Brønsted acid sites, and weak and strong Lewis acid sites, which are denoted as $B_{\text{weak}}$, $B_{\text{strong}}$, $L_{\text{weak}}$ and $L_{\text{strong}}$, respectively. The acidic properties of these catalysts depended on the preparation methods.

The densities of the acid sites and the temperatures of the maximum desorption rates (abbreviated as $T_{\text{max}}$) are summarized in Table 2. These estimates defined the weak and strong acid sites for VPO-org and VPO-redu as the acid sites below and above 650 K of the desorption temperatures, respectively, whereas this temperature was defined as 620 K for VPO-aq.

Table 2  Densities of Acid Sites and Temperature of Maximum Desorption Rate$^{a)}$ Measured by Dimethylpyridine-temperature Programmed Desorption

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Brønsted acid$^{b)}$ [µmol m$^{-2}$]</th>
<th>Lewis acid$^{c)}$ [µmol m$^{-2}$]</th>
<th>Total$^{d)}$ [µmol m$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak$^{e)}$</td>
<td>Strong$^{e)}$</td>
<td></td>
</tr>
<tr>
<td>VPO-org</td>
<td>0.040 (595 K)</td>
<td>0.055 (695 K)</td>
<td>0.121 (605 K)</td>
</tr>
<tr>
<td>VPO-redu</td>
<td>0.031 (590 K)</td>
<td>0.025 (720 K)</td>
<td>0.104 (600 K)</td>
</tr>
<tr>
<td>VPO-aq</td>
<td>0.110 (590 K)</td>
<td>0.023 (685 K)</td>
<td>0.042 (595 K)</td>
</tr>
</tbody>
</table>

a) The figures in parentheses are temperature of maximum desorption rate.
b) Density of Brønsted acid sites was estimated from 2,6-dimethylpyridine-TPD spectra.
c) Density of Lewis acid sites was calculated by subtracting that of Brønsted acid sites from that of total acid sites.
d) Density of total acid sites was estimated from 3,5-dimethylpyridine-TPD spectra.
e) For VPO-org and VPO-redu, weak and strong acids were defined as below and above 650 K of desorption temperature, respectively, and this temperature was defined as 620 K for VPO-aq.

Niwa et al.$^{22)}$ demonstrated that $T_{\text{max}}$ is shifted toward higher temperatures with the increase in acid sites in the measurement system by ammonia-TPD, which indicates that the product of the sample weight (g) and the concentration of acid sites (µmol g$^{-1}$). In this study, these spectra were measured with the same sample weight (100 mg), so the amount of the acid sites in the measurement system was different for each experiment. The amount of $L_{\text{strong}}$ in the measurement system was as follows; VPO-aq (0.081 µmol m$^{-2}$) < VPO-org (0.096 µmol m$^{-2}$) < VPO-redu (0.138 µmol m$^{-2}$). The density of $B_{\text{strong}}$ was almost the same for VPO-redu and VPO-aq. On the other hand, the density of $B_{\text{strong}}$ on VPO-org was almost twice as high as on VPO-redu and VPO-aq.

The $T_{\text{max}}$ of $L_{\text{strong}}$ was in the following order: VPO-aq (655 K) < VPO-org (680 K) < VPO-redu (690 K). Niwa et al.$^{23)}$ demonstrated that $T_{\text{max}}$ is shifted toward higher temperatures with the increase in acid sites in the measurement system by ammonia-TPD, which indicates that the product of the sample weight (g) and the concentration of acid sites (µmol g$^{-1}$). In this study, these spectra were measured with the same sample weight (100 mg), so the amount of the acid sites in the measurement system was different for each experiment. The amount of $L_{\text{strong}}$ in the measurement system was as follows; VPO-aq (0.044 µmol) < VPO-org (0.317 µmol) < VPO-redu (0.331 µmol). This order is consistent with that of $T_{\text{max}}$. In addition to that, these amounts were roughly correlated with $T_{\text{max}}$. Therefore, it is reasonable to consider that the $L_{\text{strong}}$ of these catalysts had similar strength.
The $T_{\text{max}}$ of $B_{\text{strong}}$ was in the following order: VPO-aq (685 K) < VPO-org (695 K) < VPO-redu (720 K). In contrast, amount of $B_{\text{strong}}$ in the measurement system was as follows: VPO-aq (0.012 µmol) < VPO-redu (0.060 µmol) < VPO-org (0.176 µmol). VPO-org had almost the same $T_{\text{max}}$ as VPO-aq, but the amount of $B_{\text{strong}}$ in the measurement system on VPO-aq was about 15-times that of VPO-aq. Furthermore, VPO-org had lower $T_{\text{max}}$ than VPO-redu, whereas the total amount of $B_{\text{strong}}$ in the measurement system on VPO-org was larger than that of VPO-redu. These results indicate that the $B_{\text{strong}}$ of VPO-org was relatively weak compared to the other two catalysts.

The acidic properties of the catalysts can be summarized as follows: (1) VPO-org has a higher density of $B_{\text{strong}}$, but the $B_{\text{strong}}$ are relatively weak compared to the other two catalysts. (2) VPO-redu has a higher density of $L_{\text{strong}}$. (3) VPO-aq has fewer acid sites except for $B_{\text{weak}}$.

The bulk P/V ratios of the catalysts were almost unity, that is the stoichiometric number of (VO)$_2$P$_2$O$_7$, but the surface P/V ratios were larger than unity, indicating that there is excess phosphorus on the surface. The surface P/V ratio of VPO-aq (1.5) was higher than those of VPO-org and VPO-redu (1.2) as shown in Table 1. This is consistent with the density of $B_{\text{weak}}$ as listed in Table 2. VPO-org catalysts with various bulk P/V ratios show that the density of $B_{\text{weak}}$ increases with the surface P/V ratio$^{23}$. Therefore, $B_{\text{weak}}$ can be attributed to P-OH groups, like H$_3$PO$_4$, derived from the excess phosphorus on the catalyst surface.

The DMP-TPD spectra indicate that there are at least three types of acid sites in addition to $B_{\text{weak}}$. The Brønsted and Lewis acid sites on (VO)$_2$P$_2$O$_7$ may be attributed to P-OH groups belonging to truncated P-O bonds in terminal phosphorus tetrahedra and coordinatively unsaturated vanadium ions on the (100) planes, respectively$^8$. Although it is difficult to make reasonable assignments for these acid sites from only the data of this study, further quantitative measurement of acidic property of well-characterized (VO)$_2$P$_2$O$_7$ by the DMP-TPD method can be expected to clarify the structure of these acid sites.

### 3.3. Correlation between Acidic Properties and Catalytic Performance of (VO)$_2$P$_2$O$_7$ Catalysts

Figure 4 shows the changes in selectivity to MA as a function of the conversion of butane. VPO-redu showed the highest selectivity among these catalysts. The selectivity decreased with increased conversion, but the trends of the catalysts were greatly different. The selectivity to MA of VPO-org fell remarkably, but that for VPO-redu scarcely decreased. This decrease of the selectivity is due to consecutive oxidation of MA$^{16}$.

The catalytic data are summarized in Table 3, in which the data for catalytic activity were obtained at around 20% conversion. The extent of consecutive oxidation of MA ($\text{ECOMA}$) was defined as the difference of the selectivity between 80% and 20% of the conversion, and was calculated from Eq. (1).

$$\text{ECOMA} (%) = \text{Selectivity}_{80\%\text{ conversion}} - \text{Selectivity}_{20\%\text{ conversion}}$$

The selectivity at 20% conversion was in the following order: VPO-aq (54%) < VPO-org (60%) < VPO-redu (66%). On the other hand, ECOMA was as fol-

---

![Fig. 4 Selectivity to MA as a Function of the Conversion of Butane](image)

### Table 3 Activity and Selectivity to Maleic Anhydride in Butane Oxidation over (VO)$_2$P$_2$O$_7$ Catalysts$^a$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activity$^b$ [µmol m$^{-2}$h$^{-1}$]</th>
<th>Selectivity to maleic anhydride$^c$ [%]</th>
<th>Difference of selectivity between 80% and 20% of conversions$^d$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPO-org</td>
<td>132</td>
<td>60</td>
<td>9.2</td>
</tr>
<tr>
<td>VPO-redu</td>
<td>55</td>
<td>66</td>
<td>1.6</td>
</tr>
<tr>
<td>VPO-aq</td>
<td>70</td>
<td>54</td>
<td>4.4</td>
</tr>
</tbody>
</table>

$^a$ The reaction was carried out with 1.5% butane and 20% O$_2$ in N$_2$ (balance) at 723 K.

$^b$ Calculated from the data at around 20% of the conversion.

$^c$ Selectivity to maleic anhydride at 20% or 80% of the conversions.

$^d$ Calculated by subtracting selectivity to MA at 80% conversion from that at 20% conversion.

---

The catalytic activity of VPO-org was greater than those of the other two catalysts, but this difference could not be explained by the acidic properties, possibly because the catalytic activity is strongly affected by the redox properties of the catalyst17).

Figure 5 shows the relationship between the selectivity at 20% conversion and the density of \( L_{\text{strong}} \). The selectivity increased with increased density of \( L_{\text{strong}} \). Butane may be selectively activated on strong Lewis acid sites through abstraction of hydrogen atoms from butane, and then, the formed olefinic-like intermediate is quickly oxidized up to MA by neighboring oxygen atoms4). The trend of Fig. 5 supports this proposal, indicating that \( L_{\text{strong}} \) is important for MA formation. The higher density of \( L_{\text{strong}} \) is one of the reasons for the high selectivity of VPO-redu.

It has been considered that the V-rich sites on \((\text{VO})_2\text{P}_2\text{O}_7\), where the surface P/V ratio is relatively low, are highly active for the consecutive oxidation of MA16,24). However, the surface P/V ratio of VPO-org is the same as that of VPO-redu, as shown in Table 1. In addition, the surface P/V ratio of VPO-aq is rather higher than that of VPO-org. Therefore, it is difficult to explain the difference in the consecutive oxidation of MA as suggested in the literature. As shown in Fig. 6, a correlation between ECO\(_{\text{MA}}\) and the ratio of (density of \( B_{\text{strong}} \))/(density of \( L_{\text{strong}} \)) was observed, but no correlation with only the density of Brønsted or Lewis acid sites. If MA is readily desorbed from the surface of a catalyst, MA is not subject to consecutive oxidation. It is generally accepted that acid sites are necessary for catalytic formation of anhydride or acidic molecules over solid catalysts, because these sites promote desorption of the product25). As shown in Fig. 6, \( L_{\text{strong}} \) is likely to have a good influence for the selectivity to MA. In contrast, \( B_{\text{strong}} \) will promote the consecutive oxidation of MA. Protons are readily added to the carboxyl group of carboxylic acid derivatives, as in the Brønsted acid-catalyzed hydrolysis of ester28). The strong Brønsted acid may activate the carbonyl of MA to induce subsequently oxidation into CO\(_{\text{x}}\). Therefore, the consecutive oxidation of MA is probably more accelerated on catalysts with higher densities of \( B_{\text{strong}} \) such as VPO-org.

4. Conclusion

Acidic properties of three types of \((\text{VO})_2\text{P}_2\text{O}_7\) catalysts were investigated by DMP-TPD. VPO-org had a higher density of \( B_{\text{strong}} \) and these \( B_{\text{strong}} \) sites were relatively weak compared with the other catalysts. VPO-redu had a higher density of \( L_{\text{strong}} \). VPO-aq had fewer acid sites except for \( B_{\text{weak}} \). VPO-redu had a high selectivity to MA at low conversion, and a higher density of \( L_{\text{strong}} \). The extent of consecutive oxidation of MA is related to the ratio of (density of \( B_{\text{strong}} \))/(density of \( L_{\text{strong}} \)). \( B_{\text{strong}} \) may promote the consecutive oxidation of MA, whereas \( L_{\text{strong}} \) hinders this oxidation.

Acknowledgments

This study was partly supported by Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology, by New Energy and Industrial Technology Development Organization (NEDO), and by Japan Chemical Industry Association (JCIA).
要 旨
ジメチルピリジン昇温脱離法により測定したピロリン酸ジバナジル触媒の酸性質
およびブタン選択酸化反応に対するプロヌステッド酸、ルイス酸の役割

神谷 裕一1)，西山 寛幸2)，八代 美紀2)，豊野 鉄5)，服部 忠5)

1) 東京大学大学院工学研究科応用化学専攻，464-8603 名古屋市千種区不老町
2) 名古屋大学大学院工学研究科応用化学専攻，464-8603 名古屋市千種区不老町

2種類のジメチルピリジンをプローブとしての昇温脱離法（TPD）により、(VO)₃P₂O₅触媒の酸性質を測定した。また、プローブの選択酸化による無水マレイン酸生成反応を行った。(VO)₃P₅O₇触媒において、有機溶液中で調製したVPO-org、VOPO₃-2H₂Oの還元により調製したVPO-redu、および水溶液中で調製したVPO-aqの3種類を用いた。3.5-ジメチルピリジン（3.5-DMP）はBrønsted酸点、Lewis酸点の両方に吸着し、一方、2.6-ジメチルピリジン（2.6-DMP）は二つのメチル基の立体障害によりBrønsted酸点に選択的に吸着する。ゆえに、3.5-DMP-TPDスペクトルと2.6-DMP-TPDスペクトルから、Brønsted酸点、Lewis酸点それぞれの酸量、酸強度を求めることができる。TPDスペクトルから、(VO)₃P₂O₅触媒には、強いBrønsted酸点とLewis酸点、弱いBrønsted酸点とLewis酸点の4種類が存在することが分かった。また、酸性は触媒の調製方法により大きく異なった。VPO-orgには、より多くの強いBrønsted酸点が存在し、かつその酸点は他の触媒に比べてやや弱かった。VPO-reduには、より多くの強いLewis酸点が存在した。VPO-aqの酸量は少なかった。低転化率域での無水マレイン酸選択率は、強いLewis酸の酸量に依存した。このことから、強いLewis酸点が無水マレイン酸生成に対して重要な役割を果たしていることが示唆された。無水マレイン酸の逐次酸化によるCO₂生成に関しては、強いBrønsted酸点がこの逐次酸化を促進していることが示唆された。

References
23) Private data.