

## In Situ Raman Spectroscopic Investigation of Surface Redox Mechanism of Vanadyl Pyrophosphate

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The reversible oxidation and reduction of vanadyl pyrophosphate ( $(VO)_2P_2O_7$ ) to and from  $X_1$  phase of  $VOPO_4$  on the surface was demonstrated under the reaction conditions of *n*-butane oxidation by means of *in situ* Raman spectroscopy. This result combined with the previous *ex situ* studies<sup>1</sup> indicates

that this redox cycle is responsible for the catalytic oxidation to maleic anhydride.

$(VO)_2P_2O_7$  is an active phase for selective catalytic oxidation of *n*-butane to maleic anhydride (MA) and is the main component of industrial catalysts for this process.<sup>2</sup> It has been claimed that the redox between  $V^{4+}$  and  $V^{5+}$  phase is responsible for this reaction.<sup>3,4</sup> Volta et al.<sup>5</sup> observed the formation of active sites on  $(VO)_2P_2O_7$  during the activation by using Raman spectroscopy. However, the true active sites are still controversial.<sup>1-7</sup> Therefore, the oxidation-reduction process of  $(VO)_2P_2O_7$  is of great concern to identify the true active site and the reaction mechanism. We demonstrated in the previous study that the surface of  $(VO)_2P_2O_7$  was oxidized to  $X_1$  phase upon  $O_2$  treatment and the injection of *n*-butane pulses onto the  $X_1$  phase reduced it back to  $(VO)_2P_2O_7$  accompanying by its conversion to MA.<sup>1</sup> The  $X_1$  phase which we found before<sup>8</sup> has a structure similar to  $\delta$ - $VOPO_4$ <sup>9</sup> and  $\beta''$  phase<sup>10</sup> reported independently by other groups. These results suggest that the surface redox cycle between  $(VO)_2P_2O_7$  and  $X_1$  is involved in the catalytic oxidation. However, since most of the measurements in the previous study,<sup>1</sup> i.e., Raman spectroscopy, XRD, XPS, EXAFS, were done *ex situ*, the possible change of the surface before or during the measurements could not be excluded. To solve the problem, *in situ* measurements are very much desirable.

We wish to report here by using *in situ* Raman spectroscopy that the surface redox process between  $(VO)_2P_2O_7$  and  $X_1$  phase actually took place in a reversible way under the flow reaction conditions of the selective oxidation of *n*-butane, when the butane/oxygen ratio in the feed was varied. The high selectivity at the ordinary conditions also recovered almost

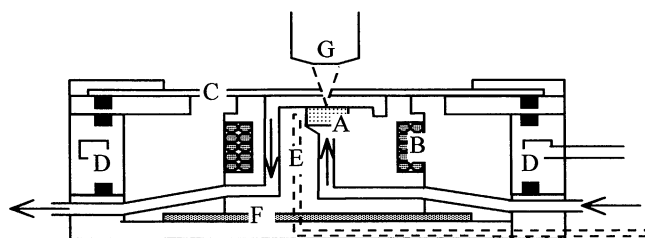
reversibly. These results indicate that this redox process is responsible for the selective MA formation.

In order to observe the changes in the structure of the catalyst under steady-state reaction conditions, an *in situ* Raman cell was constructed as illustrated in Figure 1. The arrows in the figure represent the direction of the gas flow. The sample was held in a small quartz basket, of which the bottom was made of sintered glass, A in Figure 1. This enables the reaction gas to flow upstream through the sample uniformly. The cell was cooled by circulating water (D). A thermocouple was inserted in E. F is the heat insulator. The material used for the cell was SUS 316L stainless steel, which is anti-corrosive to organic acids. With this cell, the sample can be treated at 823 K under the reaction gases. The temperature was calibrated by measuring the melting points of zinc and tin.

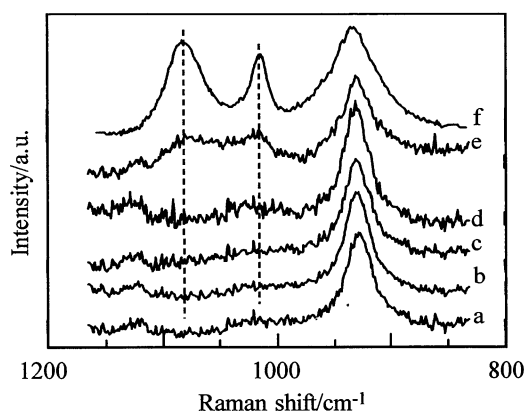
Raman spectra were recorded with a Laser Raman Spectrometer (Jasco Corporation, NR-1800) using the 514.5 nm Ar laser (NEC GLS3261J). The samples were treated under the same conditions as the steady state reaction.

$(VO)_2P_2O_7$  was obtained by the calcination of vanadium hydrogen phosphate hemihydrate ( $VOHPO_4 \cdot 0.5H_2O$ ) at 823 K in an  $N_2$  flow for 5 h (so-called organic solvent method).<sup>8,11</sup>  $X_1$  phase was synthesized from  $NH_4HVPO_6$  as described previously.<sup>8</sup>

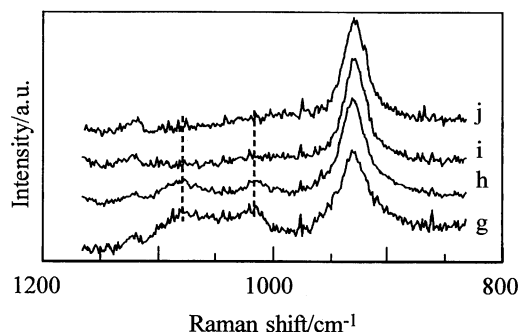
Catalytic oxidation of *n*-butane was performed in a flow reactor at 733 K. Prior to the reaction, 70 mg of catalyst was treated in  $N_2$  ( $60 \text{ cm}^3 \text{ min}^{-1}$ ) at 773 K for 1 h. First, the reaction was performed with the gas composition of *n*-butane 1.5% (17%,  $O_2$  content in parentheses). This is for the ordinary reaction conditions. Then the ratio was decreased to 0.75% (18.5%),



**Figure 1.** Schematic illustration of *in situ* Raman cell. (A) Sample, (B) heater coil, (C) quartz window, (D) cooling water, (E) thermocouple, (F) heat insulator, and (G) objective lens.



**Figure 2.** Changes in Raman spectra of  $(VO)_2P_2O_7$  under the steady state reaction. (a) the parent  $(VO)_2P_2O_7$ . Partial pressure of *n*-butane ( $O_2$ ) was decreased from (b) 1.5 (17%) to (c) 0.75 (18.5%), (d) 0.25 (19.5%), and then (e) 0 (20%), all balanced by  $N_2$ . (f)  $X_1$  phase. All spectra were recorded at 733 K.



**Figure 3.** Changes in Raman spectra of  $(\text{VO})_2\text{P}_2\text{O}_7$  under the steady state reaction. (g) The same spectrum as spectrum e in Figure 2. Partial pressure of  $n$ -butane ( $\text{O}_2$ ) was increased from 0 (20)% to (h) 0.25 (19.5)%, (i) 0.75 (18.5)%, and then (j) 1.5 (17)%, all balanced by  $\text{N}_2$ . All spectra were recorded at 733 K.

and to 0.25% (19.5%), all balanced with  $\text{N}_2$ . After this series of experiments, the catalyst was treated in a flow of air ( $20 \text{ cm}^3 \text{ min}^{-1}$ ) for 2 h. Then, the partial pressure of  $n$ -butane was increased to 0.25% (19.5%,  $\text{O}_2$  content), 0.75% (18.5%), and 1.5% (17%), all balanced with  $\text{N}_2$ . Total flow rate of the gas mixture was varied to maintain the conversion of  $n$ -butane to be  $\sim 50\%$  at each stage. In each stage of the reaction, the reaction was continued till it reached steady state.

Changes in the Raman spectra of  $(\text{VO})_2\text{P}_2\text{O}_7$  with the decrease and increase of the partial pressure of  $n$ -butane are shown in Figures 2 and 3, respectively. The selectivities of MA corresponding to each stage are summarized in Table 1. Parent  $(\text{VO})_2\text{P}_2\text{O}_7$  showed a single peak at  $930 \text{ cm}^{-1}$  (Figure 2, spectrum a), which is assigned to P-O-P stretching.<sup>12</sup> At room temperature, the P-O-P stretching mode appears at  $923 \text{ cm}^{-1}$ . With an increase in the temperature, the peak shifted to higher frequency. This is because the angle of the P-O-P is variable depending on the temperature.<sup>12</sup> After 2 h of the steady state reaction, the spectrum showed the single peak due to  $(\text{VO})_2\text{P}_2\text{O}_7$  (Figure 2, b), the MA selectivity being 52.4%. Upon the decrease of the  $n$ -butane content to 0.75%, there was little change observed either in the spectrum (Figure 2, c) or in the selectivity (48.8%). When the partial pressure of  $n$ -butane was set at 0.25%, a weak band appeared at  $1016 \text{ cm}^{-1}$  (Figure 2, d) and the selectivity decreased to 23.4%. By the subsequent oxidation by air, new peaks clearly appeared at 1016 and  $1084 \text{ cm}^{-1}$  (Figure 2, e), which are assignable to the  $\text{X}_1$  phase (Figure 2, f).  $\text{X}_1$  phase is considered to be formed on the surface of  $(\text{VO})_2\text{P}_2\text{O}_7$ .<sup>1,3</sup> The peak at  $1084 \text{ cm}^{-1}$  is probably related to V-O-P stretching,<sup>13</sup> and the peak at  $1016 \text{ cm}^{-1}$  is still unassignable. The positions and the relative intensities of the peaks are slightly different from those observed at 298 K by *ex situ* measurements.<sup>1</sup> The differences are accountable by the difference in the temperature of measurements, as was confirmed by using a pure  $\text{X}_1$  phase (see above).

Figure 3 shows the changes in Raman spectra of the  $(\text{VO})_2\text{P}_2\text{O}_7$  with the increase in the partial pressure of  $n$ -butane after the oxidation by air at 733 K, following the experiments shown in Figure 2. The spectrum g in Figure 3 is the same that e in Figure 2. As the partial pressure increased, the peaks corresponding to  $\text{X}_1$  phase decreased (Figure 3, i and j), and the selectivity recovered to 61.7%. The reaction conditions of spectrum d in Figure 2 and h in Figure 3 were the same,

**Table 1.** Changes of the selectivity to maleic anhydride over  $(\text{VO})_2\text{P}_2\text{O}_7$  with the partial pressure of  $n$ -butane

Partial pressure of $\text{C}_4\text{H}_{10}/\%$	Conversion $/\%$	Selectivity $/\%$	Raman spectrum and phase <sup>c</sup>
1.5 <sup>a</sup>	53.8	52.4	b P
0.75 <sup>a</sup>	52.0	48.8	c P
0.25 <sup>a</sup>	56.8	23.4	d P (+ X)
0.25 <sup>b</sup>	56.0	22.8	h P + X
0.75 <sup>b</sup>	51.3	44.1	i P
1.5 <sup>b</sup>	45.5	61.7	j P

<sup>a</sup> Partial pressure of butane was decreased stepwise from 1.5 (17,  $\text{O}_2$  content in parentheses)% to 0.75 (18.5)% and then 0.25 (19.5)% after  $\text{N}_2$  treatment of the catalyst at 773 K, balanced by  $\text{N}_2$ . <sup>b</sup> Partial pressure of butane ( $\text{O}_2$  content) was increased stepwise from 0.25 (19.5,  $\text{O}_2$  content)% to 0.75 (18.5)% and 1.5 (17)% after treatment under air at 733 K, balanced by  $\text{N}_2$ .

<sup>c</sup> P:  $(\text{VO})_2\text{P}_2\text{O}_7$  and X:  $\text{X}_1$ .

although the spectra are slightly different. The surface layers at the each stage of the reaction probably took a longer time to reach the steady state than the reaction itself.

These results clearly demonstrate that the oxidation of  $(\text{VO})_2\text{P}_2\text{O}_7$  to  $\text{X}_1$  by  $\text{O}_2$ , and the reduction of  $\text{X}_1$  to  $(\text{VO})_2\text{P}_2\text{O}_7$  by  $n$ -butane take place reversibly under the reaction conditions, and that the oxidation state of the surface varies depending on the relative composition of butane and oxygen.

It is notable that the change of selectivity was reversible as well and that the high selectivity (52%  $\sim$  62%) comparable with that observed under the real catalytic conditions was obtained. All these results indicate that the redox mechanism between  $(\text{VO})_2\text{P}_2\text{O}_7$  and  $\text{X}_1$  phase operates in the catalytic oxidation of  $n$ -butane, and that under the ordinary reaction conditions the  $(\text{VO})_2\text{P}_2\text{O}_7$  phase prevails on the surface.

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