***In Situ* Laser Raman Spectroscopy During Sequential Oxidizing and Reducing Conditions
for a Vanadium-Phosphorous-Oxide Catalyst**

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A VPO catalyst prepared in an organic medium has been studied by *in situ* laser Raman spectroscopy under reaction conditions for *n*-butane oxidation to maleic anhydride. Data could be obtained at low laser power and short collection times. Raman characterization during continuous flow (steady-state) studies revealed that the $(VO)_2P_2O_7$ phase was present. Sequential oxidizing (10% O_2 in N_2) and reducing (2% *n*-butane in N_2) conditions were explored at 350°C and 400°C. These cycling (unsteady-state) operations revealed that formation of α - $VOPO_4$, β - $VOPO_4$, γ - $VOPO_4$, and δ - $VOPO_4$ was enhanced during oxidizing conditions; the intensity of Raman bands due to $(VO)_2P_2O_7$ increased during reducing conditions.

Keywords: Raman spectroscopy, *in situ* cell, selective oxidation

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Introduction and background

Vanadium-phosphorus-oxygen (VPO) catalysts are used in the selective oxidation of *n*-butane to maleic anhydride. The catalyst is believed to participate in a reduction-oxidation (Mars-van Krevelen) mechanism in which: (1) the hydrocarbon and the oxide react so that the hydrocarbon becomes (partially) oxidized and the oxide becomes reduced; (2) the reduced oxide reacts with O₂ to regenerate the initial catalyst state. Maleic anhydride production from *n*-butane is particularly demanding since a 14 electron oxidation is performed by the catalyst through the abstraction of eight hydrogen atoms and the insertion of three oxygen atoms.

Recently, the use of a circulating fluidized bed reactor has been discussed in which the reduction and oxidation steps of the catalytic cycle can be separated (Contractor and Sleight, 1988). A riser section operating at 350-420°C converts *n*-butane to products accompanied by reduction of the catalyst. Re-oxidation of the catalyst is achieved in a regenerator using gas phase oxygen. Continuous recirculation of the VPO catalyst is possible in this system.

The ability of VPO catalysts to selectively oxidize *n*-butane has led to extensive studies of the preparation and characterization of specific phases; included have been (preferred) organic medium and solid state preparations (Cavani et al., 1984; Cavani et al., 1985; Moser and Schrader, 1985; Moser et al., 1987). Particular emphasis has been placed on the vanadyl pyrophosphate phase, (VO)₂P₂O₇, which is believed to be the most active phase in the VPO system (Bordes, 1987). However, because of the complexity of industrial catalysts (including the possible transformation of phases under catalytic conditions), attempts have been made to examine (VO)₂P₂O₇ and other phases using *in situ* spectroscopic techniques. Other catalyst

systems have demonstrated the utility of laser Raman spectroscopy for performing such studies (Stencil, 1990).

The first use of *in situ* laser Raman spectroscopy to study VPO catalysts was reported by Moser and Schrader (1985) who used a rotating controlled atmosphere cell in conjunction with a scanning laser Raman spectrometer. A crystalline $(VO)_2P_2O_7$ phase was prepared for these studies by the solid state reaction of $NH_4H_2PO_4$ and V_2O_5 . The *in situ* data indicated that the $(VO)_2P_2O_7$ material was stable for 8 hours at 475°C in a flow of 1.5% *n*-butane and 9% O_2 in N_2 . Strong peaks were observed at 923, 934, and 1187 cm^{-1} ; a number of much weaker peaks could be detected at 802, 963, 1003, 1023, 1051, 1128, 1140, 1168, and 1199 cm^{-1} . Moser and Schrader (1987) performed additional *in situ* LRS studies in a controlled atmosphere cell resembling a small cylindrical (glass) packed bed reactor. Experiments at 550°C with 1.5% butane in air confirmed the results of the previous study: the intense band of the vanadyl pyrophosphate phase (930 cm^{-1}) was observed. The possible formation of V(+5) phases under (severe) oxidizing conditions was also examined. Oxygen flow after 12 hours at 550°C induced a clearly observable change in the spectrum: distinct peaks due to β -VOPO₄ were present at 598, 651, 895, 987, and 1069 cm^{-1} , and lower intensity peaks were observed at 320, 369, and 435 cm^{-1} . Lashier and Schrader continued the *in situ* studies in an investigation of the reduction of β -VOPO₄ (Lashier et al., 1990). For a flow of 2% *n*-butane in He at 500°C, extensive reduction of the catalyst occurred in about 30 minutes, based on the detection of $(VO)_2P_2O_7$.

Recently, new work has appeared dealing with Raman characterization of VPO catalysts prepared by an aqueous synthesis (Abdelouahab et al., 1992). These researchers employed an *in situ* rotating lens cell operating at temperatures up to 445°C; data was apparently obtained by

accumulating 30 to 100 scans over an unspecified collection time. The emphasis of this investigation was the evolution of Raman spectra for the activation of $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ as it transformed to $(\text{VO})_2\text{P}_2\text{O}_7$ between room temperature and reaction conditions. These researchers also interpreted some of their results in terms of the possible formation of other phases, including $\alpha_{\text{II}}\text{-VOPO}_4$, $\gamma\text{-VOPO}_4$, and $\delta\text{-VOPO}_4$. Interconversion of some phases was reported: at 440°C using 2.4% butane in air, transformation of $\delta\text{-VOPO}_4$ to $\alpha_{\text{II}}\text{-VOPO}_4$ was observed. In this study, only one *in situ* spectrum for $(\text{VO})_2\text{P}_2\text{O}_7$ was presented, corresponding to conditions stated as 430°C using a 2.4% butane/air mixture. Three peaks due to this phase were present at 931, 1125, and 1176 cm^{-1} .

In more recent work, these researchers reported studies of the transformation of the catalytic precursor $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ to active VPO materials (Hutchings et al., 1994). $(\text{VO})_2\text{P}_2\text{O}_7$ and other phases were detected during heating to *in situ* conditions. For studies at 394°C in a 1.5% butane/air atmosphere, several additional broad bands were reported after 20 hr which were attributed to specific phases. The presence of the $(\text{VO})_2\text{P}_2\text{O}_7$ phase was indicated by a strong peak at 928 cm^{-1} and weaker peaks at 1126 and 1169 cm^{-1} . A low intensity band at 990 cm^{-1} was assigned to $\alpha_{\text{II}}\text{-VOPO}_4$. A very weak band at 1029 cm^{-1} was believed to be related to $\gamma\text{-VOPO}_4$. Another band at 1085 cm^{-1} could be characteristic of the α_{II} , δ , or γ phases. Attempts were made to modify the *in situ* conditions by including reaction products in the gas flow. However, the presence of water or maleic anhydride led to a severe loss of Raman intensities: even detection of the relatively strong bands for $(\text{VO})_2\text{P}_2\text{O}_7$ was not possible. The authors attributed the absence of a Raman signal to a "disordering" of the sample.

We have recently re-initiated our *in situ* investigations of VPO catalysts, using materials prepared according to typical (organic medium) industrial techniques. We have examined the catalyst *in situ* during continuous flow of reactants; we have also been interested in probing sequential oxidizing and reducing conditions which might be appropriate for the circulating fluidized bed industrial process. Such Raman studies are now feasible since recent advances in instrumentation and other techniques allow rapid collection of data. The application of *in situ* Raman techniques to an investigation of this unsteady-state catalytic process has not been previously reported.

Experimental

An *in situ* laser Raman spectroscopy cell (Figure 1) was used which had a resistive heating system capable of reaching 1000°C (Lu and Schrader, 1995). Various gas mixtures could be flowed over the catalyst sample. Using a specially designed optical mount with translators for the x-y-z directions, precise adjustment of the cell position was possible. The laser incident angle with respect to the sample could be adjusted between 0° and 90°; a 45° angle was used in these experiments. This compact cell design used a small amount of catalyst sample (approximately 10 mg) which was pressed inside a 2 mm diameter dimple on a 1 cm² aluminum plate.

A Spex Triplemate spectrometer with a cryogenic charge coupled detector (CCD) (Princeton Instruments) was used to obtain the data using the 514.3 nm line of an argon ion laser. Spectra of the catalyst were taken during "start-up" and during *in situ* operation using only 40

mW of laser power. At short collection times, this power did not induce changes in the catalyst structure. Sequential acquisition of individual spectra, rather than long-term accumulation of data, allowed a significant increase in the speed of data collection. Each spectrum was collected in 3 minutes, unless otherwise noted.

A $(VO)_2P_2O_7$ catalyst prepared by an organic route was used in these experiments. The catalyst was prepared using vanadium pentoxide and anhydrous phosphoric acid in isobutanol and benzyl alcohol (Horowitz et al., 1988).

The sample was loaded into the *in situ* cell at 25°C with ultrapure N_2 flowing at 60 sccm. Heating of the system was then begun at 5 °C/min until 350°C was reached. A mixture of 2% *n*-butane with 10% O_2 in N_2 was introduced at a flow of 60 sccm. For studies at 400°C, the increase in the reaction temperature was achieved in 15 min following start-up. After 3 hr of continuous gas flow at a constant temperature, *in situ* spectra were obtained.

In situ experiments were conducted at oxidizing or reducing conditions at 350°C and 400°C. The catalyst was sequentially exposed to an atmosphere of 10% O_2 in N_2 (oxidizing conditions) and 2% *n*-butane in ultrapure N_2 (reducing conditions) for varying periods of time. Data was taken while the catalyst was under the oxidizing or reducing atmospheres.

Results

AMBIENT CONDITIONS

Spectra were obtained at 25°C in a nitrogen atmosphere with an acquisition time of 10 minutes (Figure 2). Three peaks were clearly observed at 928, 1133, and 1186 cm^{-1} . For

previous studies of a crystalline $(VO)_2P_2O_7$ phase prepared by solid state methods (Moser and Schrader, 1985), strong bands were present at 923 (shoulder) and 934 cm^{-1} ; considerably lower intensity bands were reported at 1128 and 1187 cm^{-1} . The well-crystallized $(VO)_2P_2O_7$, synthesized by Abdelouahab et al. (1992) through an aqueous preparation, had strong bands at 921 (shoulder) and 933 cm^{-1} and very weak bands at 1126 and 1186 cm^{-1} .

CONTINUOUS FLOW *IN SITU* STUDIES

Continuous flow *in situ* studies (2% *n*-butane and 10% O_2 in N_2) were performed at 350°C and 400°C (Figure 3). After 3 hours at 350°C, *in situ* characterization revealed that the $(VO)_2P_2O_7$ phase was present: peaks were detected at 929, 1133, and 1173 cm^{-1} . After 3 hr at 400°C, bands were present at 933, 1129, and 1174 cm^{-1} which were very close to the bands expected for $(VO)_2P_2O_7$. The intensity of the 1129 cm^{-1} band was similar to the background between 1110 and 1160 cm^{-1} making the peak position somewhat difficult to determine. A broad spectral feature may be present from 975 to 1060 cm^{-1} .

RAMAN DATA ACQUISITION TIME

While maintaining conditions in the cell at 350°C with N_2 flowing, Raman spectra were recorded to determine the effect of acquisition time on peak intensities and signal-to-noise ratios. In related work, we have observed that significant changes can occur for the Raman spectra as a function of incident laser power and exposure time (Soejarto et al., 1995). Data acquisition parameters were chosen in this study so that no alterations in catalyst structure were observed (or likely) to occur. Data collection times clearly made an important difference in signal-to-noise

ratios: as a result of these studies, an acquisition time of 3 min was selected. As shown in Figure 4, $(VO)_2P_2O_7$ bands were apparent at 931, 1131, and 1178 cm^{-1} . No other VPO phases were readily observable.

CYCLING *IN SITU* STUDIES

Temperatures of 350 and 400°C were selected for the oxidizing-reducing cycling experiments since catalyst transformations may be somewhat slower under these conditions, especially at the lower temperature. A higher signal-to-noise ratio generally could be achieved as the temperature was reduced. (These operating temperatures may be at the lower limit of industrial conditions.) Only the spectral features between 800 and 1300 cm^{-1} are reported here since several characteristic peaks for the various VPO phases are present in this region.

During the oxidizing and reducing experiments at 350 and 400°C (as shown in Figures 5 and 6), a number of VPO phases could be observed; peak positions for these experiments are listed in Tables 1 and 2. Bands due to $(VO)_2P_2O_7$ were clearly detected at about 930, 1125, and 1175 cm^{-1} . β -VOPO₄ appeared to be present, as indicated by bands at about 890 and 975-980 cm^{-1} . Previous studies (Moser and Schrader, 1985; Abdelouahab et al., 1992) have reported strong bands for this phase at 895 and 985 cm^{-1} . The low-intensity band at about 975-980 cm^{-1} may also correspond to the medium intensity peak of α_{II} -VOPO₄ (979 cm^{-1}) or the weak intensity peak of δ -VOPO₄ (977 cm^{-1}). At 350°C (Figure 5(e)), a weak band at 954 cm^{-1} may correlate with the γ -VOPO₄ phase (951 cm^{-1}), but observation of this peak was not definitive. The spectra also tended to have a broad feature from about 1050 to 1115 cm^{-1} . The β -VOPO₄ phase has a strong peak at 1075 cm^{-1} which could contribute to this broad band. However, it may also

involve the strong bands located at 1091 cm^{-1} for α_{II} -VOPO₄ and 1096 cm^{-1} for γ -VOPO₄; the medium intensity 1090 cm^{-1} peak of δ -VOPO₄ could also be included (Abdelouahab et al., 1992). If these phases were present, additional very strong bands would be expected at 945 cm^{-1} for α_{II} -VOPO₄ and 936 cm^{-1} for δ -VOPO₄. Although intense, the 930 cm^{-1} peak for this catalyst is not "sharp" (FWHM of 20 cm^{-1}) compared to previously reported spectra (FWHM of 11 cm^{-1}) for a highly crystalline (VO)₂P₂O₇ (Moser and Schrader, 1985 and 1987). Therefore, the expected high intensity bands for α_{II} -VOPO₄ and δ -VOPO₄ may be obscured.

Noticeable changes in the band intensities were visible as cycling occurred between oxidizing and reducing conditions. At 350°C spectra were taken at various times in the oxidizing-reducing cycle and a 3 min acquisition time appeared to be sufficiently low to capture recurring changes in the catalyst. A decrease in the (VO)₂P₂O₇ peak intensities ($930, 1175\text{ cm}^{-1}$) was observed upon oxidation; this intensity loss was reversed with reduction. Intensities of bands assigned to V(+5) phases including α_{II} -VOPO₄ ($975\text{-}980, 1050\text{-}1115\text{ cm}^{-1}$) and β -VOPO₄ ($895, 975\text{-}980, 1050\text{-}1115\text{ cm}^{-1}$) behaved in an opposite manner: oxidation increased the intensities of these bands, while reduction resulted in a loss of intensity. At 350°C the intensity changes were most evident with the peak located at 975 cm^{-1} , while at 450°C the 895 cm^{-1} band more clearly illustrates this variation.

Discussion

The Raman spectrum of the organically synthesized catalyst has peak positions similar to those presented by Moser and Schrader (1985) and Abdelouahab et al. (1992) for (VO)₂P₂O₇.

Some differences in peak location is expected since uncertainty may be as high as 4 to 6 cm^{-1} for the current spectrometer system (nominally 2 cm^{-1}). Catalysts prepared through solid state reactions, organic phase preparations, and aqueous syntheses have quite similar Raman spectra during reaction conditions. Signal-to-noise ratios may vary among the reported data because of different acquisition times. Vanadyl pyrophosphate peak positions were observed at 928, 1133, and 1186 cm^{-1} for room temperature spectra. The 923 (shoulder) and 934 cm^{-1} $(\text{VO})_2\text{P}_2\text{O}_7$ bands previously reported (Moser and Schrader, 1985; Abdelouahab et al., 1992) appeared to correlate with the 930 cm^{-1} band of this catalyst.

During *in situ* flow, no new phases were apparent in the vanadyl pyrophosphate spectrum for time periods up to 3 hr. A shift from 1186 to 1175 cm^{-1} was observed, perhaps demonstrating some change in the structure of the catalyst at reaction temperature. Additionally, the 1133 cm^{-1} band was somewhat weaker and tended to be obscured by the background intensity in the 1110 to 1160 cm^{-1} region. Moser and Schrader (1985) reported no change in the Raman spectra of a $(\text{VO})_2\text{P}_2\text{O}_7$ phase synthesized by solid state methods after being heated to 475°C in a flow of 1.5% hydrocarbon in air for up to 8 hr. Abdelouahab et al. (1992) also reported no change in the spectra of a $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst that was prepared through aqueous means when reacting at 430°C with a 2.4% butane/air flow.

The strong $(\text{VO})_2\text{P}_2\text{O}_7$ band at 930 cm^{-1} decreased in intensity during oxidation and increased in intensity during reduction. Likewise, the $(\text{VO})_2\text{P}_2\text{O}_7$ bands at about 1130 and 1175 cm^{-1} behave in similar fashion. Vanadyl pyrophosphate was the most prevalent phase during both oxidizing and reducing conditions.

The 895 cm^{-1} band of $\beta\text{-VOPO}_4$ increased in intensity during oxidizing conditions. At 400°C , the band disappeared during reducing conditions. The intensity of the $975\text{-}980\text{ cm}^{-1}$ band, attributed to $\beta\text{-VOPO}_4$, $\alpha_{\text{II}}\text{-VOPO}_4$, or $\delta\text{-VOPO}_4$, increased in intensity during oxidizing conditions, while decreasing in intensity during reducing conditions. Abdelouahab et al. (1992) observed a transformation of $\delta\text{-VOPO}_4$ to $\alpha_{\text{II}}\text{-VOPO}_4$ under catalytic conditions; therefore, it is most likely that this band is not due to $\delta\text{-VOPO}_4$, but rather denoted the presence of either $\alpha_{\text{II}}\text{-VOPO}_4$ or $\beta\text{-VOPO}_4$. A low intensity band located at 954 cm^{-1} (Figure 5(e)) indicated the presence of $\gamma\text{-VOPO}_4$.

A broad feature located about the $1050\text{-}1115\text{ cm}^{-1}$ region was clearly evident in most spectra: during oxidation there was an increase in intensity, while during reduction the intensity decreased. The broad band located about the $1050\text{-}1115\text{ cm}^{-1}$ region was expected to involve features for the $\alpha_{\text{II}}\text{-VOPO}_4$, $\delta\text{-VOPO}_4$, $\gamma\text{-VOPO}_4$, and $\beta\text{-VOPO}_4$ phases. The simultaneous presence of these phases may be responsible for the broad, poorly distinguishable peaks present in this region during oxidizing and reducing cycling, and it seems that assignment of this region to V(+5) phase material is appropriate.

Using *in situ* XRD at 480°C in 1.7% *n*-butane-air flow for more than 4 hr, it has previously been reported that only amorphous V(+5) phases were present for catalysts prepared by aqueous and organic methods (Overbeek et al., 1994). Following reaction, these catalyst were characterized as being $(\text{VO})_2\text{P}_2\text{O}_7$. However, previous *in situ* Raman spectroscopy studies clearly show the presence of $(\text{VO})_2\text{P}_2\text{O}_7$ at reaction conditions (Moser and Schrader, 1987). Our *in situ* cycling experiments provide evidence that vanadyl pyrophosphate is present at reaction conditions, and reversible transformations to V(+5) were observed only under cycling conditions.

Post-catalytic characterization by X-ray diffraction has previously been used to demonstrate a partial phase transformation of $(VO)_2P_2O_7$ (organic preparation) to α_{II} -VOPO₄ above 380°C with 1.5% *n*-butane in air after several hours (Matsuura, 1984). Additional evidence exists for the reversible transformation of $(VO)_2P_2O_7$ to β -VOPO₄ under severe oxidizing and reducing conditions (Moser and Schrader, 1987; Lashier et al., 1990). This data verify our results which demonstrate the presence of V(+5) phases during oxidizing conditions, such as α_{II} -VOPO₄ and β -VOPO₄.

Conclusion

During unsteady state operation, *in situ* laser Raman spectroscopy can be used to directly observe changes that occur in VPO catalysts. The cycling experiments were conducted on the order of minutes, and the spectra were remarkably different from the steady-state results. Evidence for the presence of $(VO)_2P_2O_7$, α_{II} -VOPO₄, β -VOPO₄, γ -VOPO₄, and δ -VOPO₄ was sufficient to suggest their involvement in the working catalyst.

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TABLE 1

In situ Raman bands for oxidizing-reducing studies at 350°C (cm⁻¹).

Figure 5(a)	Figure 5(b)	Figure 5(c)	Figure 5(d)
890 w	890 w	891 m	892 m
930 s	927 s	930 s	934 s
			954 w
974 w	975 w	974 w	978 m
1040-1110 w, br	1040-1105 m, br	1050-1115 w, br	1045-1115 m, br
1126 w	1123 w	1129 w	1120-1137 w, br
1174 s	1175 m	1179 s	1174 m

TABLE 2

In situ Raman bands for oxidizing-reducing studies at 400°C (cm⁻¹).

Figure 6(a)	Figure 6(b)	Figure 6(c)	Figure 6(d)
	894 w		888-895 w, br
929 s	931 s	929 s	933 s
975-983 w	975-983 w	972-978 w	976-986 w, br
1060-1120 w, br	1050-1120 m, br	1050-1110 w, br	1040-1115 m, br
1130 w	1129 w	1120-1134 w, br	1124-1139 w, br
1174 s	1173 m	1175 s	1172 w

Figure 1 — *In situ* reactor cell for laser Raman spectroscopy.

Figure 2 -- Raman spectrum of $(VO)_2P_2O_7$ at 25°C with 10 min. acquisition time.

Figure 3 -- Continuous flow *in situ* spectra in 2% *n*-butane with 10% O₂ in N₂ at reaction temperatures of: (a) 350°C for 3 hr, (b) 400°C for 3 hr.

Figure 4 -- Collection time effects on signal intensity at 350°C with N₂ atmosphere. (a) 10 min; (b) 3 min; (c) 1 min.

Figure 5 -- Cycling *in situ* study at 350°C. (a) Starting material has previously undergone 30 min in oxidizing conditions and 30 min in reducing conditions; (b) at 1 min in cycle (total oxidizing time under 10% O₂ in N₂ of 5 min); (c) at 25 min in cycle (total reducing time under 2% *n*-butane in N₂ of 28 min); and (d) at 40 min in cycle (7 min of oxidizing time).

Figure 6 -- Cycling *in situ* study at 400°C. (a) Starting material has previously undergone 30 min in oxidizing conditions and 30 min in reducing conditions; (b) at 7 min in cycle (total oxidizing time under 10% O₂ in N₂ of 16 min); (c) at 23 min in cycle (total reducing time under 2% *n*-butane in N₂ of 16 min); and (d) at 42 min in cycle (10 min of oxidizing time).

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