# Effect of promoters for $n$-butane oxidation to maleic anhydride over vanadium–phosphorus-oxide catalysts: comparison with supported vanadia catalysts

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The oxidation of $n$-butane to maleic anhydride was investigated over model Nb-, Si-, Ti-, V-, and Zr-promoted bulk VPO and supported vanadia catalysts. The promoters were concentrated in the surface region of the bulk VPO catalysts. For the supported vanadia catalysts, the vanadia phase was present as a two-dimensional metal oxide overlayer on the different oxide supports ($TiO_2$, $ZrO_2$, $Nb_2O_5$, $Al_2O_3$, and $SiO_2$). No correlation was found between the electronegativity of the promoter or oxide support cation and the catalytic properties of these two catalytic systems. The maleic anhydride selectivity correlated with the Lewis acidity of the promoter cations and oxide supports. Both promoted bulk VPO and supported vanadia catalysts containing surface niobia species were the most active and selective to maleic anhydride. These findings suggest that the activation of $n$-butane on both the bulk and supported vanadia catalysts probably requires both surface redox and acid sites, and that the acidity also plays an important role in controlling further kinetic steps of $n$-butane oxidation.

Keywords: $n$-butane oxidation, maleic anhydride, VPO catalysts, promoters, supported vanadia catalysts

## 1. Introduction

Oxidation of $n$-butane to maleic anhydride over the vanadium–phosphorus-oxide (VPO) catalysts is still the only industrial catalytic process for partial oxidation of an alkane. Metal ion and oxide promoter species are frequently used in various commercial VPO catalyst formulations [1,2]. Many crystalline $V^{III}$–$V^{V}$ phosphate and promoter phases have been observed in the bulk VPO catalysts depending on the method of preparation and the limitations of the bulk characterization technique employed (e.g., XRD versus Raman). As a result, the recent literature demonstrates the lack of consensus about the active and selective phase in $n$-butane oxidation to maleic anhydride [3–12]. However, experimental results support the conclusions that the best VPO catalysts preferentially expose the (100) planes of $(VO)_2P_2O_7$ and that the bulk vanadyl pyrophosphate serves as a support for this active surface [9,10,13–15]. The recent models for $n$-butane oxidation to maleic anhydride are based on the vanadyl dimers present in the (100) plane of vanadyl pyrophosphate [9,16,17].

We have recently studied $n$-butane oxidation to maleic anhydride over model supported vanadia catalysts in order to investigate the similarities between the unpromoted bulk VPO and supported vanadia catalysts [18]. Such a study was particularly valuable, since unlike the bulk VPO catalysts, the model supported vanadia catalysts possessed surface molecular structures that could be reliably established by a variety of spectroscopic techniques [19]. The results of this study suggested the critical involvement of the bridging V–O–support bond in $n$-butane oxidation. Moreover, this oxidation reaction was more efficient when multiple surface vanadia sites were present as adjacent neighbors at high coverages, which is similar to the proposed models of $n$-butane oxidation over the bulk VPO catalysts [9,16,17].

The selectivity of the supported vanadia catalysts to maleic anhydride correlated with the Lewis acid strength of the oxide supports as well as metal oxide promoters (e.g., $P_2O_5$, $Nb_2O_5$, and $WO_3$). An especially high selectivity to maleic anhydride was observed when V–O–P bonds were formed after addition of $P_2O_5$ in accordance with previous observations [20,21]. These findings indicate that the supported vanadia catalysts represent a suitable model system capable of providing insights into the mechanism of $n$-butane oxidation over bulk VPO catalysts.

The purpose of this paper is to study the promoter effect and further elucidate the structure–reactivity relationships for $n$-butane oxidation to maleic anhydride on well-defined promoted VPO and supported vanadia catalysts.

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## 2. Experimental

### 2.1. Synthesis

The bulk model organic VPO precursor, $VOHPO_4 \cdot 0.5H_2O$, was prepared by a two-step method [22]. According to this method, $V_2O_5$ was first reacted with $H_3PO_4$ and $VOPO_4 \cdot 2H_2O$ obtained was subsequently reduced to $VOHPO_4 \cdot 0.5H_2O$ by refluxing in isobutanol. The catalytic precursor phase prepared by this method was transformed thermally into the catalytic vanadyl pyrophosphate, $(VO)_2P_2O_7$, in 1.2 vol% $n$-butane in air at 673 K. Prior to this transformation, low levels (ca. 0.25 wt%) of promoter elements (Si, Ti, Zr, and V alkoxides, Aldrich, Inc.) dissolved in anhydrous ethanol were introduced via incipient wetness impregnation of $VOHPO_4 \cdot 0.5H_2O$ in a dry nitrogen atmosphere followed by drying overnight at room temperature. A reference unpromoted $VOHPO_4 \cdot 0.5H_2O$ precursor was prepared by a similar incipient wetness impregnation method using anhydrous ethanol.

### 2.2. Characterization

The powder X-ray diffraction, Raman and BET procedures have been previously described [23]. The XPS analysis was performed using a model DS800 XPS surface analysis system (Kratos Analytical Plc.).

### 2.3. Kinetic tests

During kinetic tests, ca. 1 g of the promoted model organic precursor, $VOHPO_4 \cdot 0.5H_2O$, was placed into a U-tube Pyrex glass reactor inside an aluminum split block. The reactor was heated in the flowing 1.2% $n$-butane in air to 673 K, after which the kinetic data were collected at 653 K for up to 400 h under the catalytic reaction conditions. All experiments were carried out in once-through integral mode. The reaction was run under conditions where diffusional limitations could be neglected [23]. The effluent stream was analyzed by on-line gas chromatography. The details of the GC method may be found elsewhere [23].

## 3. Results

The XRD patterns and Raman spectra of the bulk VPO precursors as well as the fresh and equilibrated catalysts, which showed the presence of only $VOHPO_4 \cdot 0.5H_2O$ and $(VO)_2P_2O_7$, respectively, are not shown here. These bulk characterization techniques did not detect the presence of any other microcrystalline VPO or promoter phases in the bulk VPO catalysts. The 921 $cm^{-1}$ Raman band of pyrophosphate was observed at 924 $cm^{-1}$ in the model organic catalysts, which was previously associated with the presence of some $VOPO_4$ phase [23]. The intensity ratio of the "interlayer" to in-plane reflection of $(VO)_2P_2O_7$, $I_{200}/I_{042}$, which is frequently used as an indicator of the crystal morphology and disorder [23] showed little variation among the promoted catalysts. The $(VO)_2P_2O_7$ phase in these catalysts possessed a thin platelet morphology that can be observed in the SEM pictures (see figure 2 in [10]). These platelets preferentially exposed the (100) planes, which have been proposed to contain the active and selective sites for $n$-butane oxidation according to several recent models [9–12]. Based on the SEM observations, the surface (100) planes accounted for nearly 90% of the total surface area of these catalysts. The surface areas of the VPO catalysts were low (ca. 4.5 $m^2$/g), reflecting the large size of the platelet crystals. The promoter surface coverage was calculated based on several assumptions. It was assumed that the promoters were completely localized at the surface and formed a square close-packed lattice of the surface metal oxide phase. Significant surface enrichment in the promoter elements was indeed confirmed by the XPS surface measurements of the Si- and Nb-promoted VPO catalysts (see table 1). The Si-promoted catalyst showed higher surface enrichment in the promoter element than the Nb-promoted catalyst despite the lower silica content. The promoter surface coverage was estimated from the knowledge of the quantity of the promoter applied, the surface area of the promoted VPO catalysts and the promoter metal–oxygen bond distance. The average metal–oxygen bond distances were taken from the published crystal structure data [24] for the corresponding metal oxides: $d(Si–O) = 1.609$, $d(Ti–O) = 1.930$, $d(V–O) = 2.024$, $d(Nb–O) = 2.105$,

Table 1
The effect of promoters on $n$-butane oxidation to maleic anhydride on bulk VPO catalysts at 653 K in 1.2 vol% $n$-butane in air.[a]

| Promoter (M) | Wt (g) | Flow ($cm^3 min^{-1}$) | $C_4$ conv. (mol%) | $S_{MA}$ (mol%) | TOF $\times 10^{-5}$ (s) | | $\Theta$ | $R_M$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | | $C_4$ | MA | | |
| None | 0.29 | 15.5 | 20 | 35 | 53 | 19 | 0 | – |
| EtOH | 0.34 | 14.4 | 21 | 37 | 40 | 15 | 0 | – |
| Si | 0.49 | 15.7 | 23 | 47 | 39 | 18 | 0.14 | 29 |
| Ti | 0.36 | 16.1 | 13 | 16 | 36 | 6 | 0.26 | nc |
| Zr | 0.36 | 18.2 | 20 | 11 | 62 | 7 | 0.25 | nc |
| V | 0.35 | 12.3 | 19 | 36 | 43 | 16 | 0.26 | nc |
| Nb | 0.35 | 25.0 | 17 | 53 | 80 | 43 | 0.26 | 19 |

[a] Wt is the catalyst weight; MA maleic anhydride; $\Theta$ the promoter surface coverage; $R_M$ the ratio of the promoter concentration in the 2–4 nm surface region (XPS) to its total concentration; nc, not collected.
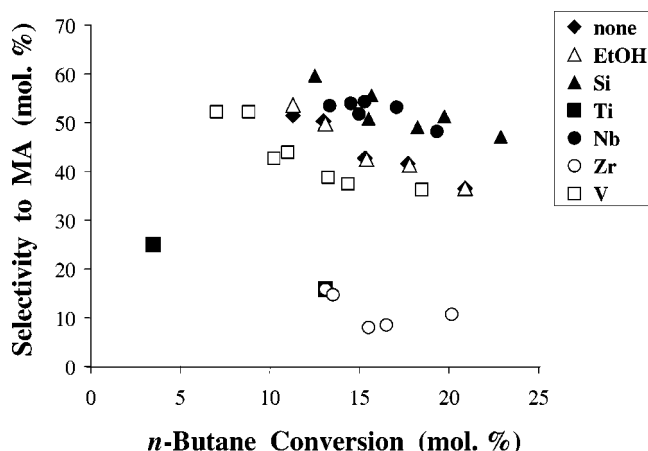
Figure 1. Catalytic performance of promoted bulk VPO catalysts in 1.2 vol% $n$-butane in air at 653 K.

and $d(\text{Zr–O}) = 2.195$ Å. As can be seen in table 1, the estimated promoter surface coverages are very close to 0.25 monolayer with the exception of the Si-promoted catalyst which had a slightly lower coverage ($\Theta = 0.14$).

The results of $n$-butane oxidation over a number of promoted model organic VPO catalysts are shown in figure 1 and summarized in table 1. The model organic VPO catalysts displayed lower selectivity to maleic anhydride as compared to the conventional organic VPO catalysts [23]. The presence of some $VOPO_4$ phase suggested by the Raman band shift of pyrophosphate [23] may be responsible for the inferior catalytic performance of the model organic system. The time required to reach the steady state did not appreciably vary among the promoted VPO catalysts of this study and was ca. 240 h under catalytic reaction conditions. The reaction rates were calculated assuming a pseudo-first-order reaction [9]. Maleic anhydride and carbon oxides were the main oxidation products detected. The thin platelet morphology of the bulk VPO system was particularly suitable for studying fundamental structure–catalytic property relationships of this system. In the present study, the relationship between the catalytic activity and the number of the surface vanadium ions present in the crystallographic (100) planes of vanadyl pyrophosphate ($5.034 \times 10^{18}$ m$^{-2}$ [25]) corrected for the promoter surface coverage was investigated. Both the catalytic activity and selectivity to maleic anhydride were significantly affected by the presence of the promoters. As can be seen in table 1 and figure 1, only the Zr- and Nb-promoted bulk VPO catalysts possessed $n$-butane oxidation activity superior to that of the unpromoted catalysts, and only the Si- and Nb-promoted catalysts were more selective to maleic anhydride.

## 4. Discussion

The promoter elements were introduced in the present bulk VPO catalysts by the impregnation of the $VOHPO_4 \cdot 0.5H_2O$ precursor at a level that was too low for the promoters to have a structural effect. Therefore, according to

a classification proposed by Hutchings [1], these promoted bulk VPO catalysts belong to the type 2 systems. Recent studies suggested that the bulk VPO promoters present at a low level may (i) function as selective poisons which block unselective surface sites present in the surface (001) planes of $(VO)_2P_2O_7$ [26,27], (ii) enhance oxidation of $V^{IV}PO$ phases into $V^VOPO_4$ in fresh catalysts, which accelerates the attainment of the steady state and optimizes the surface $V^{5+}/V^{4+}$ distribution [28], (iii) form $((VO)_xM_{1-x})_2P_2O_7$ solid solutions, which display improved catalytic properties [1], and (iv) lead to preferential exposure of the (100) planes of $(VO)_2P_2O_7$ in equilibrated catalysts via intercalation and cleavage of the hydrogen phosphate layers in the catalyst precursor structure, $VOHPO_4 \cdot 0.5H_2O$ [29].

In the present note, the likely mechanism of promoter action in the present bulk VPO catalysts as well as the similarities between the promoted bulk VPO and supported vanadia catalysts in partial oxidation of $n$-butane are discussed.

### 4.1. Promotion by poisoning unselective surface sites

This mechanism may be discerned by observing a decrease in the rate of $n$-butane oxidation upon addition of an otherwise catalytically inactive promoter as the selectivity to maleic anhydride is improved at fixed catalytic reaction conditions. Examination of the kinetic data in table 1 suggests that the poisoning of the unselective sites, such as those associated with the presence of $VOPO_4$ phases, may only play a role in the case of the bulk VPO catalyst promoted with silica, which by itself is inert in this hydrocarbon oxidation. However, the $n$-butane TOF frequency for the Si-promoted VPO catalyst was similar to that of the EtOH-treated VPO catalyst. This observation may indicate the limitations of the present TOF data to very accurately reflect the catalytic activity of these promoted VPO catalysts. The catalytic performance data for the other promoted bulk VPO catalysts shown in table 1 do not support this mechanism of promoter action.

### 4.2. Formation of oxidized phases and rapid attainment of steady state

None of the fresh or equilibrated bulk VPO catalysts showed the presence of microcrystalline oxidized $VOPO_4$ phases by XRD or Raman. Moreover, the time required to reach the steady state did not appreciably vary among promoted bulk VPO catalysts. Therefore, this mechanism of promoter action does not appear to be important for the promoted bulk VPO catalysts of this study.

### 4.3. Solid solution versus intercalation

The intercalation of the promoters into the layered structure of the $VOHPO_4 \cdot 0.5H_2O$ precursor and the cleavage of its (010) planes should result in an increase of the surface area and preferential exposure of the (100) planes of

$(VO)_2P_2O_7$ [29]. However, the surface area and relative exposure of the (100) planes of $(VO)_2P_2O_7$ in the catalysts of the present study remained essentially unchanged. Furthermore, the promoter elements in the most active and selective Nb- and Si-promoted catalysts were concentrated in the surface region. The Si-promoted catalyst was characterized by a much higher $R_M$ ratio than the Nb-promoted catalyst despite the lower promoter content, which probably indicates higher solubility of the Nb promoter in the VPO matrix. Therefore, it appears that the promoter elements may partially form a solid solution. However, this process is primarily limited to the surface region and affects the catalytic properties of the bulk VPO catalysts.

### 4.4. Promoted bulk VPO versus supported vanadia catalysts

Previously, it was concluded that the bridging V–O–support bonds were the kinetically critical functionalities in the selective oxidation of butane to maleic anhydride. The catalytic activity of the supported vanadia catalysts was found to be a very strong function of the specific metal oxide support. However, the catalytic activity of the supported vanadia catalysts did not correlate with the Sanderson [30] or Pauling [31] electronegativity of the metal cation of the oxide support. Similar to the supported vanadia system, the catalytic activity of the promoted bulk VPO system did not correlate with the above-mentioned electronegativity scales. The bulk VPO catalyst treated with the acidic Nb promoter was the most active and selective, which suggests that the surface acidity plays an important role in $n$-butane oxidation (see below). The treatment of the unpromoted bulk VPO precursor with anhydrous alcohol had a somewhat negative effect on the catalytic activity of the unpromoted bulk VPO catalyst (table 1) and no effect on its surface area. The surface areas of all equilibrated catalysts of the present study remained relatively constant at ca. 4.5 $m^2 g^{-1}$ within the accuracy of the BET method. Similar alcohol treatment in an earlier study [29] resulted in a significant improvement in the surface area and catalytic properties of the unpromoted bulk VPO system. It is possible that such treatment in the earlier study [29] facilitated removal of some inactive surface components, such as $VO(H_2PO_4)_2$ or excess orthophosphoric acid.

The maleic anhydride selectivity trends revealed that the electronegativity properties [30–32] of the promoter or bridging V–O–support bond were not related to selectivity, since the selectivity trends were Nb > Si = unpromoted > V > Ti > Zr and Al > Nb > Ti > Zr [18] for the promoted bulk VPO and supported vanadia catalysts, respectively. However, these selectivity trends parallel the strength of the Lewis acidity of the oxide supports and promoter cations, since alumina possesses the strongest Lewis acid sites followed by niobia [33]. The other supports and promoter cations of this study possessed only weak Lewis

acidity. The silica overlayers were inert in $n$-butane oxidation, and the improvement of selectivity to maleic anhydride observed in this case was possibly due to selective blockage of surface sites responsible for the total oxidation of $n$-butane. The V-, Ti-, and Zr-promoted bulk VPO catalysts possessed the catalytic activity similar to the unpromoted bulk VPO system. However, these promoter cations were less selective in $n$-butane oxidation to maleic anhydride. These observations indicated the importance of surface acidity for high activity and selectivity of the bulk VPO and supported vanadia catalysts for selective oxidation of $n$-butane. Moreover, the acidic Nb promoter had greater beneficial effect on the catalytic performance than the unselective site-poisoning effect of the Si promoter. Similarly, Zazhigalov et al. [34] observed a correlation between the selectivity to maleic anhydride and the surface acidity of the promoted bulk VPO catalysts. According to Zazhigalov et al. [34], moderate surface acidity facilitates desorption of maleic anhydride and prevents its complete oxidation to carbon oxides. In fact, the acidic promoters, such as Nb, employed in this study had a beneficial effect on the selectivity to maleic anhydride over bulk VPO and supported vanadia catalysts, suggesting that these promoters play a crucial role in controlling further kinetic steps of $n$-butane oxidation.

According to several recent models of the active surface sites [9,16,17], pairs of active surface vanadium sites present in the (100) plane of vanadyl pyrophosphate were required for selective oxidation of $n$-butane on bulk VPO catalysts. Centi et al. [9] found that the rates of hydrocarbon oxidation on the bulk VPO catalysts correlated with the process of simultaneous abstraction of two methylene hydrogen atoms and proposed an active site for butane oxidation based on vanadyl dimers present in the (100) plane of vanadyl pyrophosphate. The multiple surface vanadia sites present at ca. 0.75 monolayer coverage of vanadia on $TiO_2$ were indeed more efficient at oxidizing $n$-butane to maleic anhydride than the isolated surface vanadia sites present at lower surface coverages in the vanadia/$TiO_2$ system [18]. Further enhancement in catalytic activity and selectivity to maleic anhydride in the model vanadia/$TiO_2$ system was observed when an acidic metal oxide, $Nb_2O_5$, was present at the surface of the $V_2O_5/TiO_2$ catalyst ($\Theta_{Nb} = 0.44$, $\Theta_V = 0.17$, see table 2 in [18]). These findings suggest that the efficiency for maleic anhydride formation on supported vanadia catalysts might be related to the presence of two adjacent surface vanadia sites or a combination of a surface vanadium oxide redox and surface acid sites. Similar to the Nb-promoted supported vanadia system, the Nb-promoted bulk VPO catalyst ($\Theta_{Nb} = 0.26$) displayed the highest activity and selectivity among the bulk VPO catalysts. The observed similarities in the catalytic behavior between the supported vanadia and promoted bulk VPO catalysts suggest that selective oxidation of $n$-butane on the bulk VPO catalysts may also require a Lewis or Brønsted acid site in combination with a surface vanadium redox site [18,35].

## 5. Conclusion

In this investigation, the nature of the promoter effect in VPO catalysts was addressed employing model bulk VPO and supported vanadia catalysts. Surface acidity (surface Nb species, –POH groups at superstoichiometric P/V ratios [9]) had a positive effect on both the rate of $n$-butane oxidation and selectivity to maleic anhydride over the model bulk VPO and supported vanadia systems. This suggests that the activation of $n$-butane on both the bulk VPO and supported vanadia catalysts may require a pair of active sites (a redox and an acid site), and that the acidity also plays an important role in controlling subsequent kinetic steps of this oxidation. Moreover, they suggest that promoters play an important role in controlling the surface acidity of promoted bulk VPO and supported vanadia catalysts, which is crucial for selective oxidation of $n$-butane to maleic anhydride. The results of this work further demonstrate that the supported vanadia catalysts represent a suitable well-defined model system for bulk VPO catalysts.

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