# Molecular Structure-Reactivity Relationships in *n*-Butane Oxidation over Bulk VPO and Supported Vanadia Catalysts: Lessons for Molecular Engineering of New Selective Catalysts for Alkane Oxidation

V.V. Guliants[a]*, J. B. Benziger[b], S. Sundaresan[b], and I. E. Wachs[c]

[a]Department of Chemical Engineering, University of Cincinnati,
Cincinnati, OH 45221-0171
[b]Department of Chemical Engineering, Princeton University,
Princeton, NJ 08544
[c]Department of Chemical Engineering, Zettlemoyer Center for Surface Studies,
Lehigh University, Bethlehem, PA 18015

The present study addresses the nature of the promoter effect in the bulk VPO and supported vanadia catalysts. No correlation was found between the electronegativity of the promoter or oxide support cation and the catalytic properties of these two catalytic systems. The enhancement of surface acidity had a beneficial effect on both the rate of *n*-butane oxidation and selectivity to maleic anhydride over the bulk VPO and supported vanadia catalysts. These findings suggested that the activation of *n*-butane on both the bulk and supported vanadia catalysts may require both a redox and an acid site. The results of the present study further demonstrate that the supported vanadia catalysts represent a suitable model for bulk VPO catalysts.

## 1.    INTRODUCTION

The partial oxidation of *n*-butane to maleic anhydride over the bulk VPO catalysts is the only known commercial process for an alkane oxidation. Vanadyl(IV) pyrophosphate, $(VO)_2P_2O_7$, displaying preferential exposure of the (100) crystal planes is critical for active and selective VPO catalysts [1, 2]. The catalytic activity of the bulk VPO catalysts is confined to a very thin surface region of the (100) planes of $(VO)_2P_2O_7$ [3, 4], suggesting similarities between the bulk VPO and supported catalysts. The vanadyl dimers present in the hypothetical surface (100) planes of $(VO)_2P_2O_7$ have been suggested as the active sites for *n*-butane oxidation to maleic anhydride [1, 5-7].

Supported vanadium(V) oxide catalysts have recently attracted attention as promising model catalysts for selective oxidation of *n*-butane [8]. Unlike the bulk VPO catalysts, the model supported vanadia catalysts possessed the surface molecular structures that could be reliably established by a variety of spectroscopic techniques [9]. The recent study [10] suggested the critical involvement of the bridging V-O-support bond, and particularly V-O-P bond in *n*-butane oxidation. Moreover, this oxidation reaction was more efficient when multiple surface vanadia sites were present at high coverages, which is similar to the proposed models of *n*-butane oxidation over the bulk VPO catalysts [1, 5-7]. These findings indicate that as a model system, the supported vanadia catalysts can provide 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.

## 2. EXPERIMENTAL
### 2.1. Synthesis

The model bulk organic VPO precursor, $VOHPO_4x0.5H_2O$, was prepared by a two-step method [11] and transformed thermally into $(VO)_2P_2O_7$ in 1.2 vol. % $n$-butane in air at 673K. Prior to this transformation, 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 $VOHPO_4x0.5H_2O$. The details of this preparation method may be found elsewhere [10]. A reference unpromoted $VOHPO_4x0.5H_2O$ precursor was prepared by a similar impregnation method using anhydrous ethanol.

The supported vanadia catalysts were prepared by the incipient-wetness impregnation of the metal oxide supports ($SiO_2$, $TiO_2$, $ZrO_2$, $Nb_2O_5$, and $Al_2O_3$) with a vanadium isopropoxide solution in methanol (Alfa, 95-99% purity) [10].

### 2.2. Characterization

The powder X-ray diffraction, Raman and BET procedures have been previously described [2]. The XPS analysis was performed using a Model DS800 XPS surface analysis system (Kratos Analytical Plc.).

During kinetic tests, ca. 1 g of promoted $VOHPO_4x0.5H_2O$ or supported vanadia catalyst was placed into a U-tube Pyrex glass reactor inside an aluminum split block. The kinetic study was conducted in 1.2% $n$-butane in air at 653K and 494K for the promoted VPO and supported vanadia catalysts, respectively. The details of the kinetic tests and product analysis may be found elsewhere [2].

## 3. RESULTS

The XRD patterns and Raman spectra of the bulk model organic VPO precursors as well as the fresh and equilibrated catalysts showed the presence of only $VOHPO_4x0.5H_2O$ and $(VO)_2P_2O_7$, respectively, and are not shown here. The pyrophosphate Raman band was observed at 924 $cm^{-1}$, suggesting the presence of some $VOPO_4$ phase [2]. 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 [2] 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 (Figure 2 in [5]). 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 [1, 5, 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 (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 [13] for the corresponding metal oxides. The estimated promoter surface coverages (Table 1) are very

close to 0.25 monolayer with the exception of the Si-promoted catalyst which had a slightly lower coverage ($\Theta$=0.14).

Table 1
The effect of promoters on *n*-butane oxidation to maleic anhydride (MA) on bulk VPO catalysts at 653K in 1.2 vol.% *n*-butane in air.

| Promoter (M) | Wt. (g) | Flow (cc/min) | Conv(C4) (mol.%) | S(MA) (mol.%) | C4 TOF ($10^{-5}$/s) | MA TOF ($10^{-5}$/s) | $\Theta$ | R |
|---|---|---|---|---|---|---|---|---|
| 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 |

**Note:** Wt. is the catalyst weight; $\Theta$, the promoter surface coverage, **R**, the ratio of the promoter concentration in the 2-4 nm surface region (XPS) to its total concentration; nc, not collected.

The results of *n*-butane oxidation over a number of promoted VPO catalysts are summarized in Table 1. The model organic VPO catalysts displayed lower selectivity to maleic anhydride as compared to the conventional organic VPO catalysts [2]. The presence of some $VOPO_4$ phase suggested by the Raman band shift of pyrophosphate [2] 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. 240h under catalytic reaction conditions.
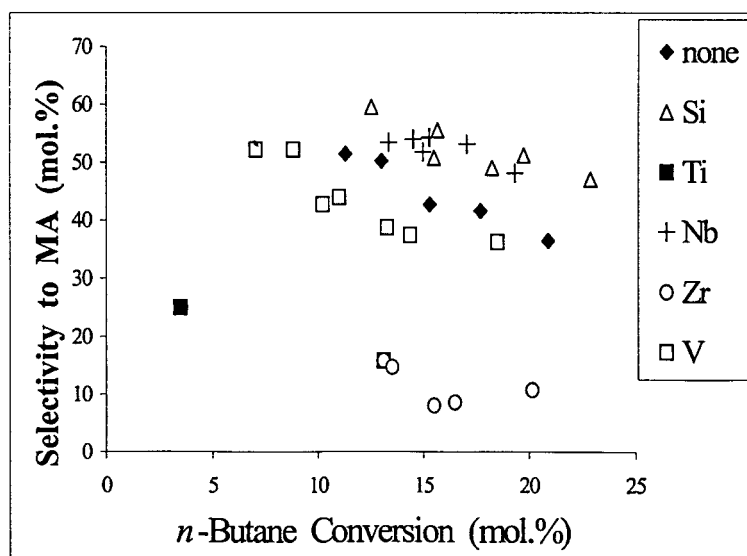


Figure 1. Catalytic performance of the bulk VPO catalysts in oxidation of *n*-butane to maleic anhydride in 1.2 vol.% *n*-butane in air at 653K.

The reaction rates were calculated assuming a pseudo-first order reaction [1]. 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 ($5.034 \times 10^{18}/m^2$ [14]) 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 (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 $VOHPO_4 x 0.5H_2O$ precursor at a level that was too low for the promoters to have a structural effect. Therefore, according to a classification proposed by Hutchings [15], 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 function as selective poisons which block unselective surface sites present in the surface (001) planes of $(VO)_2P_2O_7$ [16, 17]. Other promoter effects have been also suggested: the enhancement of 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 [18], formation of $((VO)_xM_{1-x})_2P_2O_7$ solid solutions, which display improved catalytic properties [15], and intercalation and cleavage of the hydrogen phosphate layers in the catalyst precursor structure, $VOHPO_4 x 0.5H_2O$ which leads to preferential exposure of the (100) planes of $(VO)_2P_2O_7$ in equilibrated catalysts [19].

*Promotion by poisoning unselective surface sites* 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 promoter effect by poisoning the unselective sites 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. The catalytic performance data for the other promoted bulk VPO catalysts shown in Table 1 do not support this mechanism of promoter action. *Formation of oxidized phases* in the fresh or equilibrated bulk VPO catalysts was detected by neither XRD nor Raman. Moreover, *the attainment of the steady* was not affected by the presence of promoters in the bulk VPO catalysts. Therefore, this mechanism of promoter action does not appear to be important for the promoted bulk VPO catalysts of this study. The *intercalation of the promoters* into the layered structure of the $VOHPO_4 x 0.5H_2O$ 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 $(VO)_2P_2O_7$ [19]. 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.

*Lessons for Molecular Design of New Oxidation 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 (Table 1 in [10]). However, the catalytic activity of the supported vanadia catalysts did not correlate with the Sanderson or Pauling electronegativity of the metal cation of the oxide support [10]. 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, 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 within the accuracy of the BET method. Similar alcohol treatment in an earlier study [19] 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 [19] 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 [20] 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 [10] 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 [21]. 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. Similarly, Zazhigalov *et al.* [22] observed a correlation between the selectivity to maleic anhydride and the surface acidity of the promoted bulk VPO catalysts. According to Zazhigalov *et al.* [22], 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 [1, 5-7], 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. 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 (Figure 11 in [10]). 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$_2$O$_5$, was present at the surface of the V$_2$O$_5$/TiO$_2$ catalyst, ($\Theta_{Nb}$=0.44, $\Theta_V$=0.17 in Table 3 [10]). 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 (Table 1). 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 [10, 23].

## 5.  ACKNOWLEDGEMENT

## REFERENCES

[1]  G. Centi, F. Trifirò, J. R. Ebner, and V. M. Franchetti, Chem. Rev. 88 (1988) 55.

[2]  V. V. Guliants, J. B. Benziger, S. Sundaresan, I. E. Wachs, J. M. Jehng, and J. E. Roberts, Catal. Today 28 (1996) 275.

[3]  M. A. Pepera, J. L. Callahan, M. J. Desmond, E. C. Milberger, P. R. Blum, and N. J. Bremer, J. Am. Chem. Soc. 107 (1985) 4883.

[4]  M. Abon, K. E. Béré, and P. Delichère, Catal. Today 33 (1997) 15.

[5]  V. V. Guliants, J. B. Benziger, S. Sundaresan, N. Yao, and I. E. Wachs, Catal Lett. 32 (1995) 379.

[6]  B. Schiøtt, K. A. Jørgensen, and R. Hoffmann, J. Phys. Chem. 95 (1991) 2297.

[7]  P. A. Agaskar, L. DeCaul, and R. K. Grasselli, Catal. Lett. 23 (1994) 339.

[8]  V.V. Guliants, Catal. Today 51 (1999) 255.

[9]  I.E. Wachs and K. Segawa, Characterization of Catalytic Materials, I.E. Wachs (Ed.), Butterworths, Stoneham, MA, 1992, p. 69.

[10]  I. E. Wachs, J.M. Jehng, G. Deo, B. M. Weckhuysen, V. V. Guliants, J. B. Benziger, and S. Sundaresan, J. Catal. 170 (1997) 75.

[11]  H. Igarashi, K. Tsuji, T. Okuhara, and M. Misono, J. Phys. Chem. 97 (1993) 7065.

[12]  G. J. Hutchings, C. J. Kiely, M. T. Sananes-Schulz, A. Burrows, and J. C. Volta, Catal. Today 40 (1998) 273.

[13]  Metal oxide structure files, Cerius$^2$ version 3.8 molecular modeling package (1998), Molecular Simulations Inc., 9685 Scranton Road, San Diego, CA, 92121.

[14]  Yu. E. Gorbunova and S. A. Linde, Dokl. Akad. Nauk SSSR 245 (1979) 584.

[15]  G. J. Hutchings, Appl. Catal. 72 (1991) 1, and references therein.

[16]  I. Matsuura and M. Yamazaki, in: New Developments in Selective Oxidation, eds. G. Centi and F. Trifirò (Elsevier, Amsterdam, 1990), 563.

[17]  T. Okuhara, K. Inumaru, and M. Misono, in: Catalytic Selective Oxidation, eds. J. Hightower and S. T. Oyama (ACS, Washington, DC, 1993), 156.

[18]  J. C. Volta, Catal. Today 32 (1996) 29.

[19]  D. Ye, A. Satsuma, A. Hattori, T. Hattori, and Y. Murakami, Catal. Today 16 (1993) 113.

[20]  R. T. Sanderson, Polar Covalence (Academic Press, New York, 1983); L. Pauling, The Chemical Bond (Cornell Univ. Press, Ithaca, NY, 1967); R. G. Pearson, Inorg. Chem. 27 (1988) 734.

[21]  J. Datka, A. M. Turek, J. M. Jehng, and I. E. Wachs, J. Catal 135 (1992) 186.

[22]  V. A. Zazhigalov, J. Haber, J. Stoch, I. V. Bacherikova, G. A. Komashko, A. I. Pyatnitskaya, Appl. Catal. A 134 (1996) 225.

[23]  F. Cavani and F. Trifirò, in: 3$^{rd}$ World Congress on Oxidation Catalysis, eds. R. K. Grasselli, S. T. Oyama, A. M. Gaffney, and J. E. Lyons (Elsevier Science B.V., Amsterdam, 1997), 19.