Investigation of the Mechanism of *n*-Butane Oxidation on Vanadium Phosphorus Oxide Catalysts: Evidence from Isotopic Labeling Studies

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Abstract: The selective oxidation of *n*-butane to maleic acid catalyzed by vanadium phosphates (VPO) is one of the most complex partial oxidation reactions used in industry today. Numerous reaction mechanisms have been proposed in the literature, many of which have butenes, butadiene, and furan as reaction intermediates. We have developed an experimental protocol to study the mechanism of this reaction in which ^{13}C-isotopically labeled *n*-butane is flowed over a catalyst bed and the reaction products are analyzed using ^{13}C NMR spectroscopy. This protocol approximates the conditions found in an industrial reactor without requiring an exorbitant amount of isotopically labeled material. When [1,4-13C]*n*-butane reacted on VPO catalysts to produce maleic acid and butadiene, the isotopic labels were observed in both the 1,4 and 2,3 positions of butadiene and maleic acid. The ratio of label scrambling was typically 1:20 for the 2,3:1,4 positions in maleic acid. For butadiene, the ratio of label scrambling was consistently much higher, at 2:3 for the 2,3:1,4 positions. Because of the discrepancy in the amount of label scrambling between maleic acid and butadiene, butadiene is unlikely to be the primary reaction intermediate for the conversion of *n*-butane to maleic anhydride under typical industrial conditions. Ethylene was always observed as a side product for *n*-butane oxidation on VPO catalysts. Fully ^{13}C-labeled butane produced about 5−13 times as much isotopically labeled ethylene as did [1,4-13C]butane, indicating that ethylene was produced mainly from the two methylene carbons of *n*-butane. When the reaction was run under conditions which minimize total oxidation products such as CO and CO_2, the amounts of ethylene and carbon oxides produced from fully ^{13}C-labeled butane were almost equal. This strongly suggests that the total oxidation of *n*-butane on VPO catalysts involves the oxidation and abstraction of the two methyl groups of *n*-butane, and the two methylene groups of *n*-butane form ethylene. An organometallic mechanism is proposed to explain these results.

Introduction

The selective oxidation of *n*-butane to maleic anhydride is recognized as one of the most complex selective oxidation reactions used in industry today.[1−12] In this reaction, eight hydrogen atoms are abstracted from *n*-butane, and three oxygen atoms are added to form maleic anhydride. The selectivity to

maleic anhydride is around 65−70% under typical industrial conditions (less than 2 molar % *n*-butane in air, with conversion from 70 to 85% between 400 and 450 °C).[2] Only maleic anhydride (or acid), carbon oxides, and a trace amount of acetic acid are detected under such conditions. All catalysts used industrially for the production of maleic anhydride from *n*-butane are based on vanadium phosphorus oxides (VPO).[2] Vanadyl pyrophosphate $((VO)_2P_2O_7)$ is regarded to be the active phase of the VPO catalysts since it is the single crystalline phase that exists in equilibrated VPO catalysts (after more than 200 h on stream).[2] The average oxidation state of vanadium in equilibrated VPO catalysts is typically 4.00−4.03.[2]

Despite extensive study, little is known about the reaction mechanism for *n*-butane oxidation on VPO catalysts. One reason is that none of the potential reaction intermediates, such as butenes, butadiene, furan, etc., have been observed in the products using typical industrial conditions.[13] A common approach has been to run the reaction under unusual reaction conditions to detect possible reaction intermediates. Centi et

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(1) Birkeland, K. E.; Babitz, S. M.; Bethke, G. K.; Kung, H. H. *J. Phys. Chem. B* **1997**, *101*, 6895−6902.
(2) Centi, G.; Trifirò, F.; Ebner, J. R.; Franchetti, V. M. *Chem. Rev.* **1988**, *88*, 55−80.
(3) Centi, G. *Catal. Today* **1993**, *16*, 5−26.
(4) Cavani, F.; Trifirò, F. *Catalysis* **1994**, *11*, 246−315.
(5) Abon, M.; Volta, J.-C. *Appl. Catal.* **1997**, *157*, 173−193.
(6) Hutchings, G. J.; Kiely, C. J.; Sananes-Schulz, M. T.; Burrows, A.; Volta, J. C. *Catal. Today* **1998**, *40*, 273−286.
(7) Herrmann, J.-M.; Vernoux, P.; Béré, K. E.; Abon, M. *J. Catal.* **1997**, *167*, 106−117.
(8) Hutchings, G. J.; Sananes, M. T.; Sajip, S.; Kiely, C. J.; Burrows, A.; Ellison, I. J.; Volta, J. C. *Catal. Today* **1997**, *33*, 161−171.
(9) Aït-Lachgar, K.; Tuel, A.; Brun, M.; Herrmann, J. M.; Krafft, J. M.; Martin, J. R.; Volta, J. C.; Abon, M. *J. Catal.* **1998**, *177*, 224−230.
(10) Hutchings, G. J.; Desmartln-Chomel, A.; Oller, R.; Volta, J. C. *Nature* **1994**, *368*, 41−45.
(11) Gai, P. L.; Kourtakis, K. *Science* **1995**, *267*, 661−663.
(12) Coulston, G. W.; Bare, S. R.; Kung, H.; Birkeland, K.; Bethke, G. K.; Harlow, R.; Herron, N.; Lee, P. L. *Science* **1997**, *275*, 191−193.

(13) Centi, G.; Fornassari, G.; Trifirò, F. *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 32−37.

al.[14] have shown that at high butane concentrations, butenes, butadiene, and furan, but no maleic anhydride, were detected using a traditional flow reactor. Another approach has been nonequilibrium transient experiments which employ a temporal analysis of products (TAP) reactor developed by Gleaves et al.[15−17] The reactor consisted of high-speed injection valves, a microreactor, and a quadrupole mass spectrometer separated from the reactor by differentially pumped chambers.[15] Butenes, butadiene, and furan were detected sequentially with respect to their maximum intensity on equilibrated $(VO)_2P_2O_7$ catalyst. However, when the catalyst was first pulsed extensively with oxygen at reaction temperature (420 °C) and subsequently pulsed with *n*-butane, maleic anhydride was observed, but the proposed intermediate products were not.[15] The following reaction pathway was proposed on the basis of these results:[4,14]

 (1)
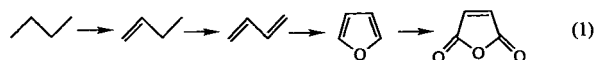
However, several arguments have been made against butenes, butadiene, and furan as reaction intermediates:[2,4]

1. These compounds were detected under very unusual conditions, such as low oxygen and very high *n*-butane concentrations and at very low contact times, or under high vacuum in the TAP reactor, or in the oxidation of *n*-butane under anaerobic conditions in a pulse reactor.

2. There was no desorption of intermediates during *n*-butane oxidation in the presence of available oxygen (either molecular oxygen or lattice oxygen associated with V^{5+}).

3. The oxidation of *n*-butane and the intermediate compounds on VPO catalysts yielded different product distributions. As mentioned above, only maleic anhydride, carbon oxides, and a trace amount of acetic acid were detected for *n*-butane oxidation. By contrast, acetaldehyde, crotonaldehyde, and other partial oxidation products were detected in the case of the oxidation of C_4 olefins.[2]

Kinetic methods have also been used to study the reaction mechanism. Zhang-Lin et al.[18] conducted kinetics studies of the oxidation of *n*-butane, butadiene, furan, and maleic anhydride on various VPO phases to investigate the mechanism of *n*-butane oxidation on VPO catalysts. They concluded that the main route from butane to maleic anhydride is an "alkoxide route" in which the precursors to maleic anhydride are alkoxide species. These alkoxides maintain a σ-bond between the substrate and the catalyst surface, and there is no desorption in the gas phase of butenes, butadiene, and furan. By using crystallochemical models of active sites and examining the energetics and geometries of butane oxidation on the (100) face of $(VO_2)_2P_2O_7$, Ziolkowski et al.[19] reported that the active site for the direct oxidation of butane to maleic anhydride is situated between four protruding, undersaturated oxygens ($2 \times V-O$, $2 \times P-O$). The activation of butane consists of the abstraction of a H from each

methyl group, with the concerted formation of two strong $C_{terminal}-O_{surf}$ bonds so that the molecule is anchored long enough for the reaction to be completed. However, experiments with deuterium-labeled *n*-butane revealed that the first step of butane oxidation is the irreversible activation of a methylene $C-H$ bond in butane on the catalyst surface.[20]

In situ Fourier transform infrared (FTIR) spectroscopy studies have been performed to investigate butane oxidation on VPO catalysts.[21,22] Wenig and Schrader used an in situ FT-IR cell to study the interaction of *n*-butane with VPO catalysts.[22] These authors reported evidence for the presence of *n*-butane, maleic anhydride, carbon oxides, and reactive surface species (maleic acid and olefins) on the catalyst at temperatures of 200−400 °C. Recently, Xue and Schrader developed a technique called "transient FTIR" which uses special operation techniques such as pulse reaction and reactant feed cycling to observe the evolution of the IR spectra as a function of time.[23] Results from transient FTIR studies suggested that unsaturated noncyclic carbonyl species may be precursors to maleic anhydride and butane might be adsorbed on the VPO catalyst to form olefinic species at low temperatures (50 °C). The latter point contradicts general observations that the activation of butane to butenes is the rate-limiting step and occurs at much higher temperature (>350 °C).[2]

Recently, we have developed an experimental protocol which utilizes selective ^{13}C isotopic labeling and examination of the reaction products by ^{13}C NMR spectroscopy to investigate the mechanism of *n*-butane oxidation on VPO catalysts. The advantage of this protocol is that the fate of the ^{13}C label can be monitored after the reaction and therefore gives insights into the reaction mechanism. Previously we have shown that the label in butadiene produced from [1,4-^{13}C]*n*-butane is completely scrambled, but in maleic acid, also produced from [1,4-^{13}C]*n*-butane, the label is largely unscrambled. This makes it unlikely that maleic acid is formed predominantly by a butadiene intermediate.[24]

In this paper, we describe our experimental results for all aspects of this reaction obtained using this protocol. We have found that ethylene was always a side product for the reaction of *n*-butane on VPO catalysts. When fully ^{13}C-labeled butane was used instead of [1,4-^{13}C]butane, the ^{13}C NMR peak intensity of ethylene increased by 5−13 times, showing that ethylene was produced mainly from the two methylene carbons of *n*-butane. Moreover, the yields of carbon oxides and ethylene were roughly equal on catalysts with phosphorus:vanadium ratios slightly higher than the stoichiometric ratio (P:V = 1.2 and 1.1). These catalysts had higher selectivities for maleic acid production. This result suggests that the total oxidation of *n*-butane on the selective VPO catalysts involves mainly the oxidation and abstraction of the two methyl carbons, and the two methylene groups are left to form ethylene. The ratio of label scrambling in maleic acid changed significantly when *n*-butane reacted on the VPO catalysts with higher P:V ratios. When the P:V ratio changed from 0.9 to 1.2, the ratio of label scrambling changed from 1:30 to 1:6 for the 2,3:1,4 positions

(14) Centi, G.; Fornasari, G.; Trifirò, F. *J. Catal.* **1984**, *89*, 44−51.
(15) Gleaves, J. T.; Ebner, J. R.; Kuechler, T. C. *Catal. Rev. Sci. Eng.* **1988**, *30*, 49−116.
(16) Rodemerck, U.; Kubias, B.; Zanthoff, H.-W.; Baerms, M. *Appl. Catal. A: General* **1997**, *153*, 203-216. Rodemerck, U.; Kubias, B.; Zanthoff, H.-W.; Baerms, M. *Appl. Catal. A: General* **1997**, *153*, 217−231.
(17) Kubias, B.; Rodemerck, U.; Zanthoff, H.-W.; Meisel, M. *Catal. Today* **1996**, *32*, 243−253.
(18) Zhang-Lin, Y.; Forissier, M.; Sneeden, R. P.; Védrine, J. C.; Volta, J. C. *J. Catal.* **1994**, *145*, 256−266. Zhang-Lin, Y.; Forissier, M.; Védrine, J. C.; Volta, J. C. *J. Catal.* **1994**, *145*, 267−275.
(19) Ziolkowski, J.; Bordes, E.; Courtine, P. *J. Catal.* **1990**, *122*, 126−150.
(20) Pepera, M. A.; Callahan, J. L.; Desmond, M. J.; Milberger, E. C.; Blum, P. R.; Bremer, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 4883−4892.
(21) Busca, G. *Catal. Today* **1996**, 457−496.
(22) Wenig, R. W.; Schrader, G. L. *J. Phys. Chem.* **1987**, *91*, 5674−5680.
(23) Xue, Z.-Y.; Schrader, G. L. *J. Catal.* **1999**, *184*, 87−104.
(24) Chen, B.; Munson, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 11024−11025.

in maleic acid. Concurrently, more ethylene was observed when [1,4-^{13}C]butane reacted on the VPO catalysts with higher P:V ratios. The correlation between the ratio of label scrambling and the peak intensity of ethylene when [1,4-^{13}C]butane was the reactant indicates that there might be an association between the formation of ethylene and the occurrence of label scrambling. There was no ethylene formed and no label scrambling was observed when butadiene reacted on the VPO catalysts to produce maleic acid. From these results we are able to propose a plausible mechanism for this reaction. We propose that *n*-butane is absorbed on the VPO catalysts via an organometallic interaction between the two methyl carbons of butane and the vanadium atom on the surface of the catalyst during the reaction, thus forming a chelating configuration. The chelating configuration serves to hold the butane molecule on the surface of the catalyst while hydrogens of butane are removed from it and oxygens are added to it until maleic anhydride is formed. The chelating configuration of the reaction intermediates is used to explain label scrambling, formation of ethylene, and other observations.

Experimental Section

Synthesis of VPO Catalysts. The catalysts used in this study can be divided into two groups: catalysts with constant P:V ratio (1:1) but different average vanadium oxidation states, and catalysts with different P:V ratios. Catalysts are denoted either by their average vanadium oxidation states, e.g., VPO3.92, or the P:V ratio, e.g., P:V = 0.9. The procedures for making these catalysts are described as follows.
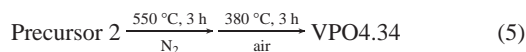
(i) Catalysts with Constant P:V Ratio (1:1). Precursor 1. Stoichiometric amounts (P:V = 1:1) of V_2O_5 and H_3PO_4 (85%) were mixed in ethanol and refluxed for 16 h. The resulting precursor was blue and identified by XRD as $VOHPO_4 \cdot 0.5H_2O$.

VPO3.92, VPO4.75, and VPO4.95 were made from precursor 1:

$$\text{Precursor 1} \xrightarrow[\text{N}_2]{550\ ^\circ\text{C, 3 h}} \text{VPO3.92} \qquad (2)$$

$$\text{Precursor 1} \xrightarrow[\text{air}]{380\ ^\circ\text{C, 3 h}} \text{VPO4.75} \qquad (3)$$

$$\text{Precursor 1} \xrightarrow[\text{air}]{450\ ^\circ\text{C, 24 h}} \text{VPO4.95} \qquad (4)$$

Precursor 2. The procedure described by Cavani et al.[25] was modified slightly. The catalysts were prepared by suspending 45 g of V_2O_5 in 90 mL of isobutyl alcohol and 60 mL of benzyl alcohol. The suspension was stirred continuously and boiled for 1 h under reflux. H_3PO_4 (85%) emulsified in 100 mL of isobutyl alcohol was then added to the cold slurry in a quantity necessary to obtain the 1:1 P:V atomic ratio, and then the slurry was boiled and stirred for 1 h. After cooling, the slurry was filtered and the powder dried at 150 °C for 10 h.

VPO4.34, VPO4.56, and VPO4.95 were made from precursor 2:

$$\text{Precursor 2} \xrightarrow[\text{N}_2]{550\ ^\circ\text{C, 3 h}} \xrightarrow[\text{air}]{380\ ^\circ\text{C, 3 h}} \text{VPO4.34} \qquad (5)$$

$$\text{Precursor 2} \xrightarrow[\text{air}]{380\ ^\circ\text{C, 3 h}} \text{VPO4.56} \qquad (6)$$

$$\text{Precursor 2} \xrightarrow[\text{air}]{450\ ^\circ\text{C, 3 h}} \text{VPO4.84} \qquad (7)$$

(ii) Catalysts with Different P:V Ratios (0.9−1.2). Catalysts with various P:V ratios were made using the following procedure: 5 g of V_2O_5 and a stoichiometric amount of H_3PO_4 (85%) (P:V = 0.9−1.2) were mixed in 100 g of isobutanol and refluxed for 24 h with continuous

(25) Cavani, F.; Centi, G.; Trifirò, F. *Appl. Catal.* **1984**, *9*, 191−202.
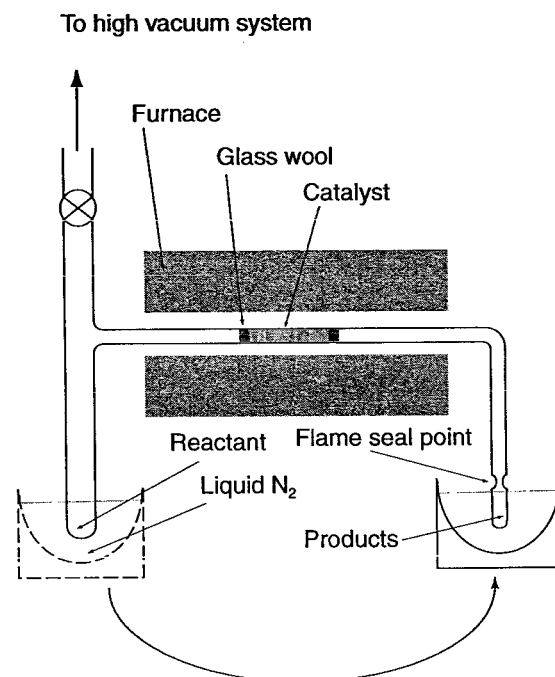
Figure 1. Pseudo-flow reactor.

stirring. The suspension was then transferred to a 1000-mL beaker and heated gently on a hot plate to near dryness. The residue was then dried at 110 °C for 24 h. The resulting precursor was calcined at 380 °C for 3 h in air to obtain the catalyst.

Characterization of the Catalysts. The average valence state of vanadium in the VPO catalysts was determined using the potentiometric method described by Niwa and Murakami.[26] Specific surface areas of the VPO catalysts were measured using the BET method (Micromeritics ASAP 2000). The XRD patterns of the catalysts were obtained using a X-ray diffractometer (SIEMENS D5005).

Pseudo-Flow Reaction. A pseudo-flow reactor was designed to prepare samples for NMR analysis (Figure 1). VPO catalyst (~0.2 g) was placed in the center of the glass reactor. The reactor was attached to a high-vacuum line and evacuated to <5 × 10^{-3} Torr. The reactants (butane or butadiene, ~50 μmol) were condensed in one end of the reactor with liquid N_2. After the catalyst was preheated in a furnace to the desired temperature, liquid N_2 was removed from the reactants and moved to the other end of the reactor. The reactants then boiled off and passed through the catalyst due to the pressure gradient induced by the liquid N_2 on the other end. After the pseudo-flow process was complete, the glass ampule containing the reaction products and the remaining reactant was flame-sealed and analyzed using NMR spectroscopy. All of the reactions reported here were run using the pseudo-flow reactor under anaerobic conditions unless otherwise denoted.

1,4- and fully ^{13}C-labeled *n*-butane were obtained from Isotec Inc. 2-^{13}C-labeled butadiene was obtained from Cambridge Isotope Laboratories. These materials are of 99% purity, and the trace amounts of impurities did not interfere with the interpretation of the experimental results.

NMR Spectroscopy. ^{13}C NMR spectra were acquired on a home-built 200 spectrometer operating at 50.197 MHz for ^{13}C. The glass ampule from the pseudo-flow reaction was placed in a zirconia rotor (7.5 mm), packed with diatomaceous earth, and sealed with Kel-F plugs. There was no detectable background signal from the diatomaceous earth. The Kel-F plugs and the Vespel spinning module give a very broad background signal from approximately 75 to 150 ppm, but this caused no difficulties in spectral interpretation. Single-pulse ^{13}C excitation (Bloch decay) with proton decoupling (pulse delay = 1−3 s, 10 000−

(26) Niwa, M.; Murakami, Y. *J. Catal.* **1982**, *76*, 9−16.

Table 1. Physical and Chemical Properties of the VPO Catalysts

catalyst	av valence state of V in fresh catalyst	crystalline phases detected by XRD	color	BET surface area, $m^2 g^{-1}$
VPO3.92	3.92	$(VO)_2P_2O_7$	brown	12.68
VPO4.34	4.34	unknown	brownish green	10.34
VPO4.56	4.56	unknown	green	13.80
VPO4.75	4.75	unknown	green	8.38
VPO4.84	4.84	unknown	green	10.34
VPO4.95	4.95	unknown	yellowish green	5.85
P:V = 1.2	4.47		dark green	
P:V = 1.1	4.57		dark green	
P:V = 1.0	4.86		green	
P:V = 0.95	4.96		yellowish green	
P:V = 0.90	4.97		yellowish green	

100 000 transients) was used to obtain all spectra presented in this contribution. Unless otherwise indicated, the spectra shown are Bloch decay spectra. All spectra were acquired at room temperature. Magic-angle spinning was used to help eliminate susceptibility effects associated with observing samples containing both gases and liquids.

Results

Catalyst Characterization. The physical and chemical properties of the VPO catalysts are listed in Table 1. Only the average vanadium oxidation state was determined for the catalysts with P:V ratios of 0.9−1.2. The XRD pattern of VPO3.92 matches very well with that of vanadyl pyrophosphate ($(VO)_2P_2O_7$). No match to a crystalline phase was found for the other catalysts, as all of these catalysts were basically amorphous. The surface areas of all of these catalysts was around 10 m^2/g, which is typical of VPO catalysts made in organic solvent.[16] For the catalysts with different P:V ratios, the oxidation state increased as the P:V ratio decreased, although their precursors had the same vanadium valence state (4.0) and the precursors were calcined under identical conditions. This is consistent with the observations in the literature that addition of phosphorus prevents the oxidation of vanadyl pyrophosphate to $VOPO_4$.[2,3]

NMR Peak Assignments. Table 2 lists the ^{13}C chemical shift assignments for the reactants, products, and intermediates observed in this study. Most of the chemical shift values listed in Table 2 were obtained from analysis of pure compounds under conditions similar to those used to analyze the pseudo-flow reaction products. While most of the chemical shifts were found to be in agreement with the previously reported values, a few discrepancies arose because no chemical shift has been reported for the species in the gas phase or in aqueous solution. For example, the literature values[27] for the chemical shifts of maleic acid (solvent: $CDCl_3$ + DMSO-d_6) are 167.2 (C1 and C4) and 130.6 ppm (C2 and C3), while the values we measured using saturated aqueous solution of maleic acid were significantly different (170.1 and 132.1 ppm). Moreover, the chemical shifts of maleic acid changed slightly with concentration (Figure 2), which might be attributed to the larger degree of dissociation at smaller concentrations. When [2,3-^{13}C]maleic acid was heated at 110 °C for 5 h (Figure 2e), another peak appeared at 135 ppm, which corresponds to the chemical shift of the 2,3 carbons of fumaric acid, indicating that part of maleic acid was converted to the trans configuration. The chemical shift assignments of

(27) Pouchert, C.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, 1st ed.; Aldrich Chemical Co., Inc.: Milwaukee, WI, 1993; Vol. 1.

Table 2. ^{13}C Chemical Shift Assignments[a] for Reactants, Products, and Intermediates Observed in This Study

product	observed ^{13}C chemical shift[b]
methane	-10.8[c]
ethane	3.5[c] (6.4)
2-*cis*-butene	9.1 (12.1), 124.8 (123.0)
1-butene	10.7 (13.1), 26.1 (27.1), 110.4 (113.1), 139.7 (140.3)
n-butane	10.8 (13.5), 24.4 (25.4)
2-*trans*-butene	14.8 (17.7), 124.9 (126.3)
propene	16.1 (18.6), 112.8 (115.0), 132.0 (133.2)
acetylene	67.3[c]
methandiol	83.0[c]
furan	107.3 (109.6), 142.0 (143.0)
butadiene	113.6 (117.1), 137.3 (138.0)
ethylene	120.0 (122.3)
benzene	127.7 (128.2)
maleic acid, disodium salt	131.6, 176.5
fumaric acid, disodium salt	131.8, 176.7
maleic acid (satd aq solution)	132.1, 170.1
fumaric acid (satd aq solution)	135.0, 170.0
CO_2	125.6[c]
CO	183.5[c]

[a] Based on literature, running reference compounds and multiplicity patterns obtained without proton decoupling and/or with ^{13}C fully labeled materials. All chemical shift values were obtained by running reference compounds at room temperature unless noted. Values in parentheses refer to chemical shifts in the liquid phase. [b] ppm from TMS. [c] From literature.
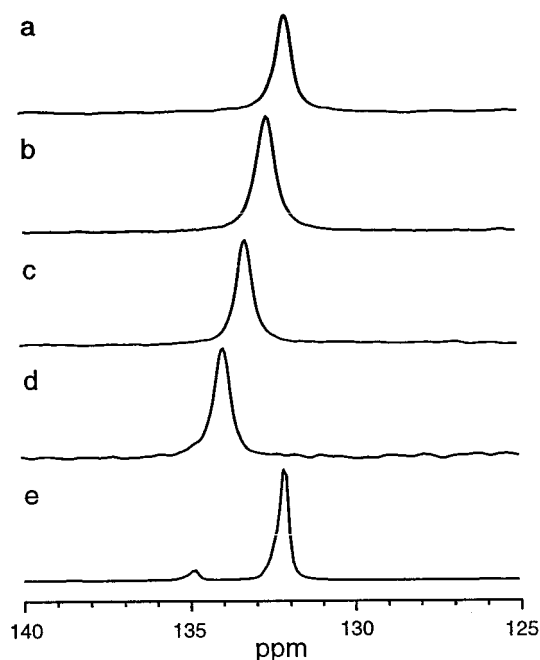

Figure 2. Chemical shift of the 2,3 carbons of maleic acid at different concentrations: (a) 1.0 M, (b) 0.27 M, (c) 0.10 M, (d) 0.016 M, (e) same concentration as (b) but heated at 110 °C for 5 h.

maleic acid and fumaric acid were further confirmed by the ^{1}H−^{13}C coupling patterns in the absence of proton decoupling and the ^{13}C−^{13}C coupling patterns when fully ^{13}C-labeled materials were analyzed.

Reaction of *n*-Butane on VPO Catalysts with Constant P:V Ratio (1:1) but Different Average Vanadium Oxidation States. The oxidation state of vanadium is the key factor that controls the product distribution of *n*-butane oxidation on VPO catalysts. Figure 3 shows the ^{13}C MAS NMR spectra of the reaction products of either [1,4-^{13}C]butane or fully ^{13}C-labeled butane flowed over a catalyst with an intermediate oxidation
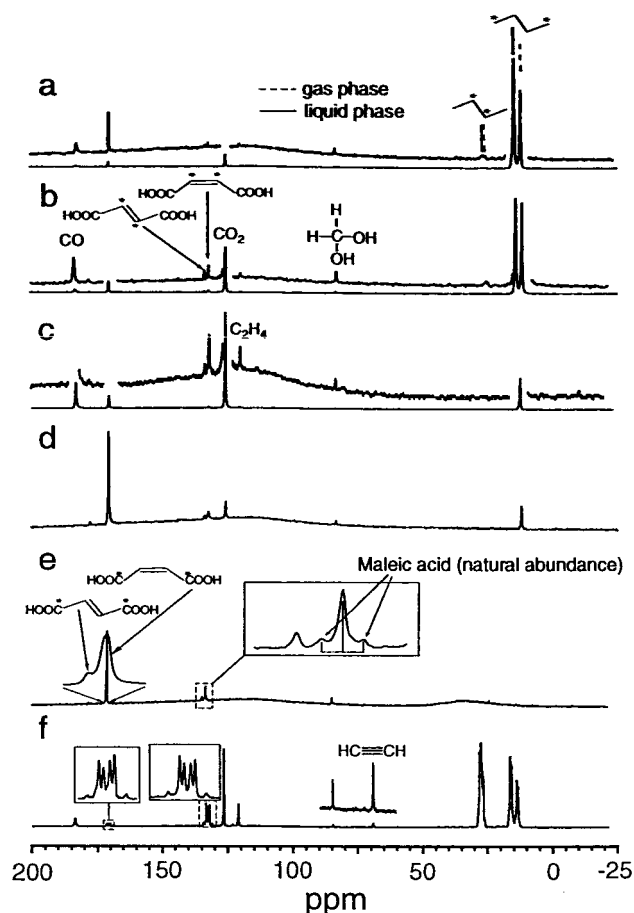
Figure 3. ^{13}C MAS NMR spectra of the reaction products of *n*-butane on VPO4.56 after reaction at various temperatures: (a) [1,4-^{13}C]butane, 330 °C; (b) [1,4-^{13}C]butane, 380 °C; (c) [1,4-^{13}C]butane, 450 °C; (d) [1,4-^{13}C]-butane, 500 °C, ampule open to air prior to sealing; (e) [1,4-^{13}C]butane, 380 °C, ampule evacuated prior to sealing; (f) uniformly ^{13}C-labeled butane, 380 °C. Spectra in (a), (b), and (c) were expanded vertically at a factor of 8, 8 and 32, respectively. The expansions for the peaks in (e) and (f) are not uniform.

state of vanadium (VPO4.56) at different temperatures. Figure 3a−c shows the reaction products of [1,4-^{13}C]butane obtained after reaction at 330, 380, and 450 °C, respectively. The product distribution was relatively independent of temperature. The largest peaks in Figure 3a,b are due to the ^{13}C-labeled C1 and C4 carbons of butane in both the liquid and gas phases. The small peaks due to natural abundance ^{13}C in the 2 and 3 positions of butane were also observed around 25 ppm in Figure 3a,b. Only CO_2, CO, and maleic acid (170 ppm, corresponding to the 1 and 4 positions) were detected as the major reaction products, which is consistent with observations in the literature.[2] Maleic acid, rather than maleic anhydride, was detected because of excess water produced from both the reaction and possibly the release of adsorbed water on the catalyst. Besides the major peaks, two minor peaks corresponding to ethylene (120 ppm) and methanediol (83 ppm) were also detected. In addition, two small peaks at 132 and 134 ppm were observed. They correspond to maleic acid (132 ppm) and fumaric acid (134 ppm), in which the labeled carbons are in the 2,3 positions.

Several experiments were performed to validate the assignment of the peaks at 132 and 134 ppm to maleic and fumaric acid, respectively. Figure 3d shows the spectrum of the reaction products of [1,4-^{13}C]butane at 500 °C when the glass ampule

was open to air prior to sealing. The largest peak corresponds to carbons in the 1,4 positions of maleic acid, because other major components such as CO, CO_2, ethylene, and butane were all gaseous species and were largely removed when the ampule was open to air. The peaks at 132 and 134 ppm remained, confirming that these peaks were produced by a nonvolatile compound. When [1,4-^{13}C]butane was reacted on VPO4.56 at 380 °C and the ampule evacuated prior to analysis (Figure 3e), all the gaseous and volatile species mentioned above were totally removed, leaving only peaks for maleic acid, fumaric acid, and methanediol in the spectrum. The peak assigned to [2,3-^{13}C]-maleic acid is bracketed by two smaller peaks assigned to the 2,3 carbons of maleic acid at natural abundance. The natural abundance carbons correspond to a doublet due to $^{13}C-^{13}C$ couplings to the ^{13}C labels in the 1 and 4 positions of maleic acid. No correlation between the relative peak intensity of maleic acid to fumaric acid was found in our studies of this reaction.

Figure 3f shows the ^{13}C MAS NMR spectrum of fully ^{13}C-labeled butane run under the same conditions as in Figure 3b. The product distribution was the same as that of the sample shown in Figure 3b, except that the peaks for ethylene and acetylene are much larger than those observed for [1,4-^{13}C]-butane, suggesting that ethylene and acetylene were produced mainly from the two methylene carbons of *n*-butane. Figure 3f also shows that the parameters used to acquire the spectrum resulted in the carbonyl resonance of maleic acid being ∼6.5 times smaller than the olefinic resonance, although the ratio should be 1:1, because NMR spectra, especially single-pulse spectra, should be quantitative. Spectra acquired with longer repetition times between acquisitions showed that the intensities of all of the other peaks observed in our experiments were quantitative. From the integrated intensity ratios of 1:5 for the carbonyl and olefinic resonances of maleic acid, respectively, in Figure 3e and using a scaling factor of 6.5, we estimate that the amount of label exchange for the sample in Figure 3e was ∼3%. This is consistent with the intensities of the natural abundance carbons (1.1%) observed in Figure 3e.

The reaction was performed on VPO catalysts with average oxidation states of vanadium ranging from 4.95 to 4.34 in order to investigate the effect of the oxidation state of the catalyst on *n*-butane oxidation. The product distributions were very similar to that of VPO4.56. Label scrambled maleic acid and fumaric acid, ethylene, and methanediol were produced on all the catalysts.

n-Butane oxidation was also carried out on VPO3.92, which contains only V^{4+} and V^{3+}, to compare product distributions on this catalyst with those on catalysts which contain V^{5+}. ^{13}C MAS NMR spectra for the reaction of [1,4-^{13}C]butane on VPO3.92 at different temperatures are shown in Figure 4. The activity of the catalyst was quite low compared to that of catalysts containing V^{5+}, as evidenced by the very small peaks of the reaction products at 450 and 500 °C (Figure 4a,b). Moreover, there were no peaks corresponding to maleic acid in all of the spectra, indicating that V^{5+} was necessary for the production of maleic acid.[6,12,16] Instead, butenes, butadiene, and furan were detected.

The most interesting reaction product was butadiene for several reasons. First, the ratio of [1,4-^{13}C]butadiene to [2,3-^{13}C]butadiene was ∼60:40. This ratio did not change signifi-
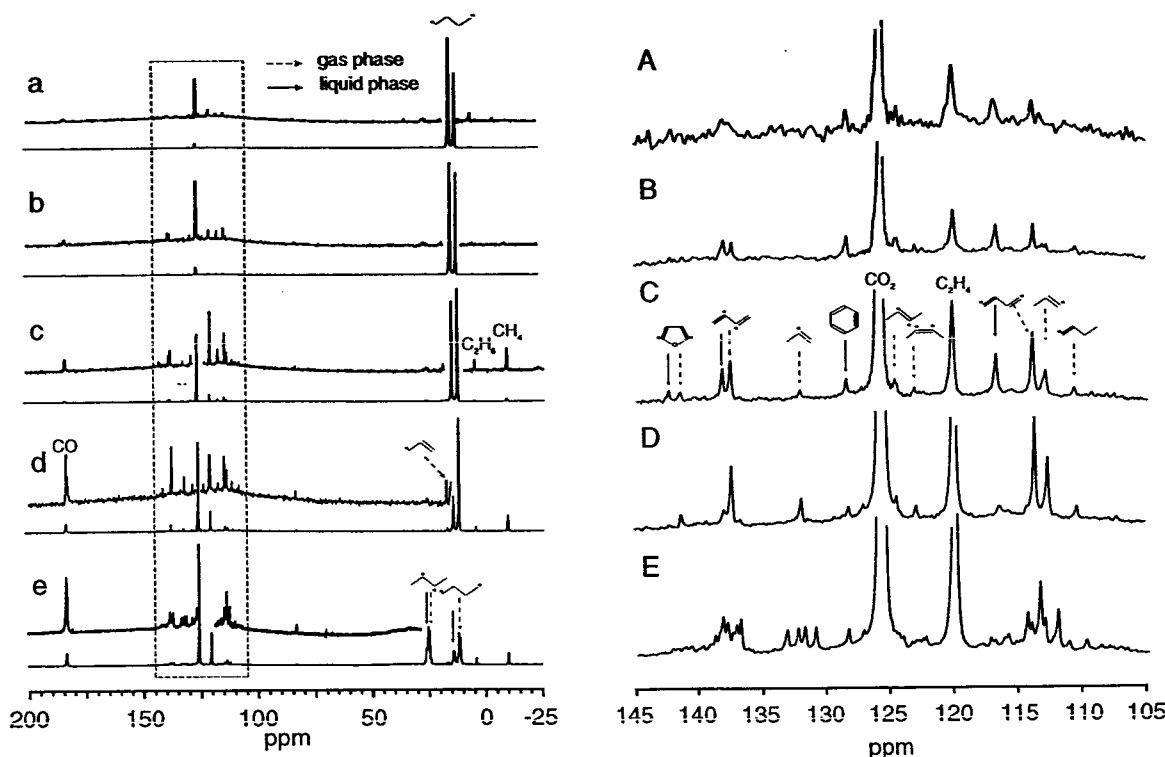
Figure 4. ^{13}C MAS NMR spectra of the reaction products of *n*-butane on VPO3.92 after reaction at various temperatures: (a) [1,4-^{13}C]butane after reaction at 450 °C; (b) [1,4-^{13}C]butane after reaction at 500 °C; (c) [1,4-^{13}C]butane after reaction at 550 °C; (d) [1,4-^{13}C]butane after reaction at 600 °C; (e) fully ^{13}C-labeled butane after reaction at 600 °C. A, B, C, D, and E are the expansions of a, b, c, d, and e, respectively.

cantly with temperature (Figure 4a−d). If butadiene produced by this mechanism was a reaction intermediate for maleic acid production, then the amount of label scrambling observed in maleic acid should be ∼40%. Because the amount of label scrambling observed for maleic acid was typically only 1−7%, this suggests that butadiene is unlikely to be a reaction intermediate in the mechanism responsible for most of the conversion of *n*-butane to maleic anhydride. Second, the peaks for butadiene are not split by ^{13}C−^{13}C spin−spin couplings. This indicates that the observed label scrambling is probably *not* produced by the formation of cyclobutane, which would produce ^{13}C labels in the 1,2; 2,3; and 1,4 positions with a 2:1:1 peak ratio. The resulting coupling pattern should be composed of a doublet due to 1,2 coupling and a singlet due to 1,4 and 2,3 carbons. Multiple couplings are observed in the spectrum of fully ^{13}C-labeled butane (Figure 4e). Because only a singlet is observed, a concerted reaction mechanism, in which the carbons in the 1,4 positions are transferred to the 2,3 positions, is more reasonable.

Ethylene was the second major product in all of the spectra shown in Figure 4. The intensity of the ethylene peak did not increase significantly when [1,4-^{13}C]butane was substituted with fully ^{13}C-labeled butane (compare spectra d and e in Figure 4). This result is quite different from that of *n*-butane oxidation on VPO4.56 (Figures 3), where only a trace amount of ethylene was detected when [1,4-^{13}C]butane was the reactant. The coincidence of a higher yield of ethylene and a higher degree of label scrambling suggests that there might be an association between label scrambling and the formation of ethylene. Methane, ethane, and propene are likely to be the cracking products of *n*-butane because they were detected in significant amounts only at 550 and 600 °C.

n-Butane Oxidation on VPO3.92 in the Presence of Gaseous Oxygen. All the reactions mentioned above were run under anaerobic conditions, which is quite different from industrial conditions (less than 2% *n*-butane in air). The industrially used VPO catalysts contain only a single crystalline phase, vanadyl pyrophosphate, which is regarded as the active phase for the selective oxidation of *n*-butane. The XRD pattern of VPO3.92 matches well with that of vanadyl pyrophosphate. To simulate industrial reaction conditions, [1,4-^{13}C]butane was oxidized on VPO3.92 at 380 °C in the presence of oxygen. Specific ratios of oxygen and *n*-butane were co-condensed in one end at the pseudo-flow reactor. Oxygen was allowed to boil off first to oxidize the catalyst while keeping *n*-butane condensed. The gaseous oxygen was then condensed in the other end of the reactor, and [1,4-^{13}C]butane was allowed to react on the catalyst. The amount of oxygen in the pseudo-flow reactor was varied, with the mole ratio of oxygen/*n*-butane being 1−22. The pressure of oxygen in the pseudo-flow reactor was calculated to be in the range of ∼0.1−2 atmospheric pressure.

The ^{13}C MAS NMR spectra for the products of these reactions are shown in Figure 5. No maleic acid was detected when the mole ratio of oxygen/*n*-butane was 1:1. For all the other oxygen/ *n*-butane ratios, maleic acid was formed, and label scrambling was observed. However, the ratio of label scrambling did not change consistently with the ratio of oxygen/*n*-butane. When the ratio of oxygen/*n*-butane increased from 3:1 to 10:1, the ratio of label scrambling decreased, which agrees with our observation that label scrambling decreases with increased oxidation state of the catalyst (vide infra). However, label scrambling increased dramatically when the oxygen/*n*-butane ratio increased from 10:1 to 22:1, and label scrambling at oxygen/*n*-butane of 22:1 was almost at the highest ratio obtained
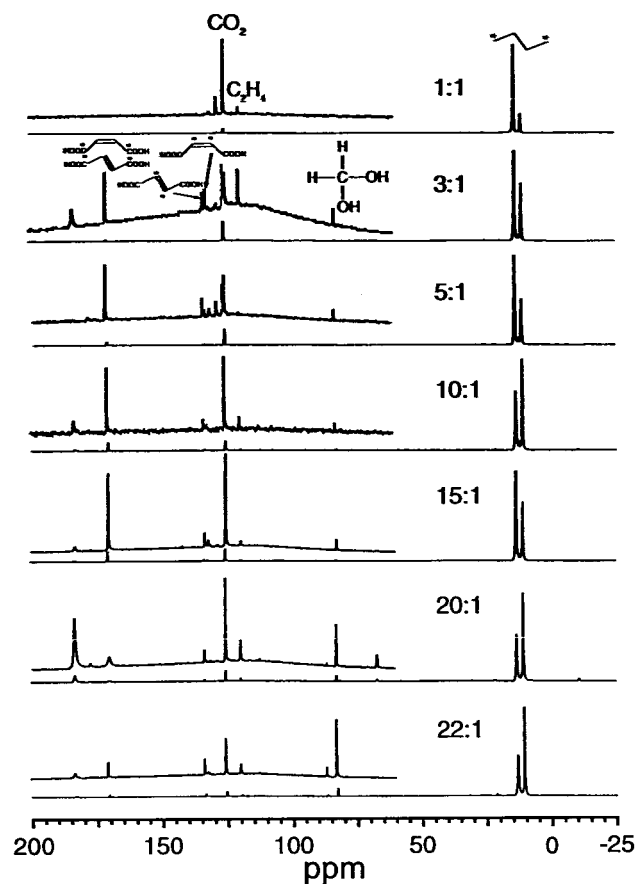
Figure 5. ^{13}C MAS NMR spectra of the reaction products of [1,4-^{13}C]-butane on VPO3.92 after reaction at 380 °C. The catalyst was oxidized under different pressures of oxygen at 380 °C for 30 min before flowing butane through the catalyst.

Figure 6. ^{13}C MAS NMR spectra of the reaction products of [1,4-^{13}C]-butane on VPO3.92 after reaction at 380 °C in the presence of gaseous oxygen (mole ratio of oxygen/butane = 10).

so far for maleic acid. However, the selectivity of the reaction toward maleic acid showed an opposite trend. The selectivity increased with the ratio of oxygen/*n*-butane and reached a maximum when oxygen/*n*-butane = 10, and then the selectivity decreased as oxygen/*n*-butane increased from 10 to 22. The cause of the increase in label scrambling at higher oxygen/*n*-butane ratios is not clear. It is likely that on the catalysts that have been oxidized by a higher concentration of oxygen (oxygen/*n*-butane > 15), total oxidation of *n*-butane dominated the reaction at the beginning. Total oxidation of *n*-butane significantly decreased the concentration of V^{5+} on the surface of the catalyst, which favored label scrambling in the subsequent selective oxidation of *n*-butane to maleic acid. Again, ethylene and methanediol were always detected. Methanediol became a major partial oxidation product at oxygen/butane ratios of 20:1 and 22:1.

The drawback of the above-mentioned approaches is that oxygen and *n*-butane react sequentially with the catalyst, which is not exactly the case with industrial reactions in fixed-bed flow reactors. Another experiment was performed to better mimic true industrial conditions. A vacuum valve was added to the pseudo-flow reactor between the reactant chamber and the catalyst. Oxygen and [1,4-^{13}C]butane (O$_2$/butane = 10) were mixed before the valve was opened. The gaseous mixture was then allowed to flow through VPO3.92 at 380 °C. Shown in Figure 6 is the ^{13}C MAS NMR spectrum of the reaction products. The formation of maleic acid, ethylene, and meth-

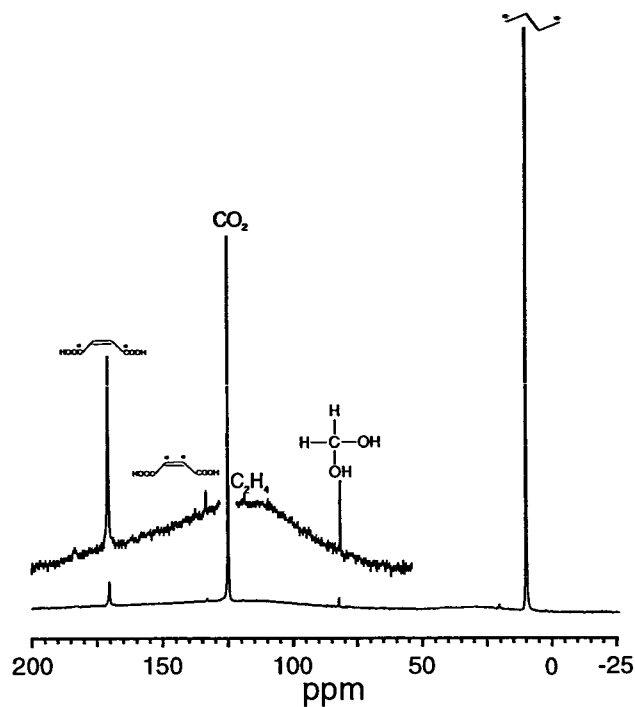anediol and label scrambling were consistent with previous results, except that the percent conversion of the reaction was much higher, showing that the presence of gaseous oxygen during the reaction enhanced the activity of the catalyst.

Effect of Oxidation State of the Catalyst on Label Scrambling. The most unexpected result that we observed was ^{13}C label scrambling in maleic acid. While the amount of label-scrambled maleic acid might be very low, it could provide valuable insight into the mechanism of the reaction. To further understand the mechanistic significance of label scrambling, the effects of various factors, such as oxidation state and P:V ratio of the catalyst, reaction temperature, etc., on label scrambling were investigated. The percentage of label exchange for maleic acid varied between 1% and 5% when the initial oxidation state of vanadium changed between 4.34 and 4.95. Because these catalysts were made from different precursors and showed different activities, it is hard to estimate the effect of the oxidation state of vanadium on label scrambling using the data from these catalysts. To simplify the situation, sequential reactions of [1,4-^{13}C]butane on VPO4.95 were performed to investigate the effect of reduction of the catalyst on label scrambling. Five sequential reactions were performed on VPO4.95 at 380 °C, and the ratio of label scrambling changed from 1:100 to 1:20 (2,3:1,4 in maleic acid) as the catalyst was reduced, showing that the lower oxidation state of the catalyst favors label scrambling.

Effect of P:V Ratio on Label Scrambling. The phosphorus-to-vanadium (P:V) ratio is a key parameter in determining the selectivity and activity of VPO catalysts.[2−4,8,28,29] A slight excess of phosphorus with respect to the stoichiometric amount (an

(28) Wenig, R. W.; Schrader, G. L. *Ind. Eng. Chem. Fundam.* **1986**, *25*, 612−620. Wenig, R. W.; Schrader, G. L. *J. Phys. Chem.* **1986**, *90*, 6480−6488.
(29) Hannour, F. K.; Martin, A.; Kubias, B.; Lücke, B.; Bordes, E.; Courtine, P. *Catal. Today* **1998**, *40*, 263−272.
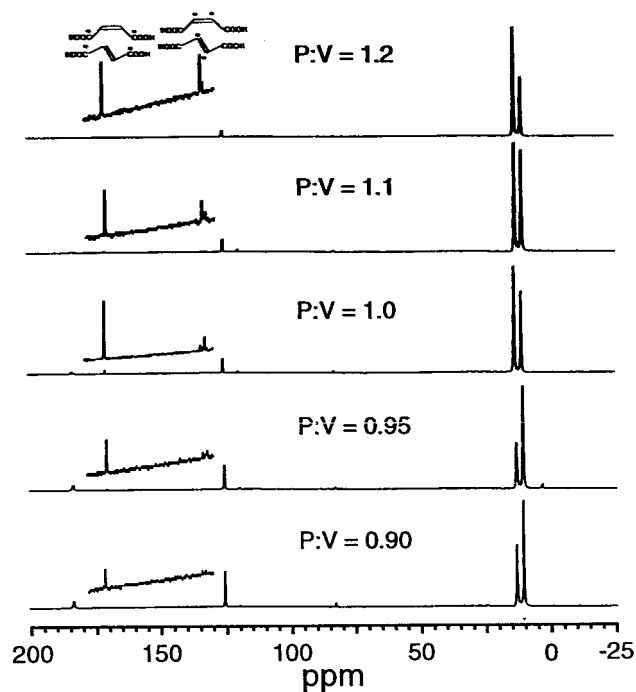
Figure 7. ^{13}C MAS NMR spectra of the reaction products of [1,4-^{13}C]-butane on the VPO catalysts with different P:V ratios. The average oxidation state of vanadium in these catalysts was 4.47−4.97 (Table 1). The reaction temperature was 380 °C.

atomic P:V ratio in the range of 1.01−1.10) was necessary to obtain an optimal catalyst.[4] For this reason the effect of P:V ratio on label scrambling was investigated. [1,4-^{13}C]Butane was allowed to react at 380 °C on VPO catalysts with P:V ratios ranging from 0.9 to 1.2. ^{13}C MAS NMR spectra of the products of these reactions are shown in Figure 7. The ratio of label scrambling in maleic acid and fumaric acid changed consistently as the P:V ratio changed from 1.2 to 0.9. When P:V = 1.2, the ratio of label scrambling was estimated to be 1:6 (2,3:1,4 in maleic acid and fumaric acid); when P:V = 0.9, the peaks from the label scrambled carbons were very small, though the signal/noise ratio does not allow an accurate estimation of the ratio of label scrambling. The precursors of the catalysts with different P/V ratios (0.9−1.2) have essentially the same oxidation state (∼4.0). However, large variations (4.47−4.97) in the oxidation state of the catalysts were obtained after the precursors were calcined under identical conditions (Table 1). It has been shown that higher oxidation states result in less label scrambling, which makes it difficult to attribute changes in the ratio of label scrambling to P:V ratio only.

When [1,4-^{13}C]butane reacted at 550 °C on the precursors of the catalysts with different P:V ratios to produce butadiene, the percentage of label-scrambled butadiene was consistently 40−45% (Figure 8). This result is consistent with our previous experiments on VPO3.92.

Formation of Carbon Oxides and Ethylene. Previous experiments showed that ethylene is always a byproduct in the oxidation of *n*-butane on the VPO catalysts. Figure 9 shows the ^{13}C MAS NMR spectra of the reaction products of fully ^{13}C-labeled butane and [1,4-^{13}C]butane on VPO catalysts with different P:V ratios. The ratios of the integrated peak intensities of ethylene and carbon oxides (CO and CO_2) from either fully ^{13}C-labeled butane or [1,4-^{13}C]butane were calculated and are shown in Figure 10. The peak intensity of ethylene increased
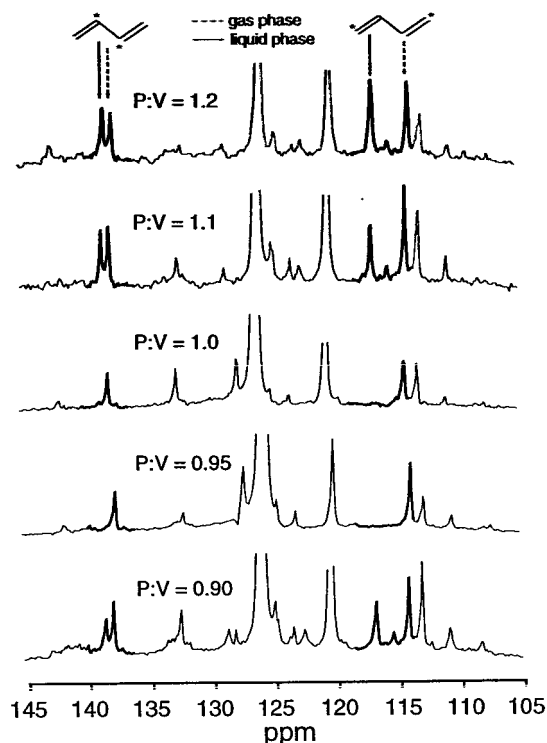

Figure 8. ^{13}C MAS NMR spectra of the reaction products of [1,4-^{13}C]-butane on the precursors of the VPO catalysts with different P:V ratios. The reaction temperature was 550 °C.
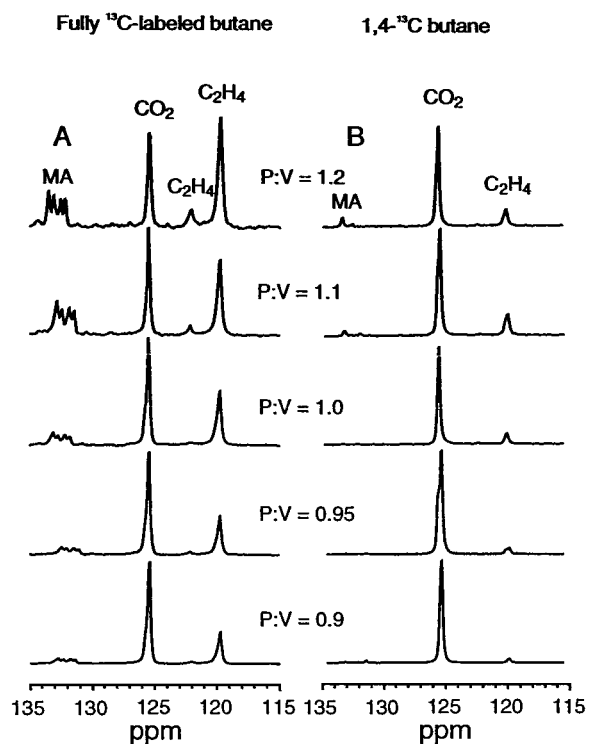

Figure 9. ^{13}C MAS NMR peaks of maleic acid (and fumaric acid), carbon dioxide, and ethylene produced from the reaction of [1,4-^{13}C]butane and fully ^{13}C-labeled butane on VPO catalysts with different P:V ratios at 380 °C: (A) fully ^{13}C-labeled butane and (B) [1,4-^{13}C]butane.

by a factor of 5−13 when fully ^{13}C-labeled butane was used instead of [1,4-^{13}C]butane. A similar result has been observed on VPO4.56 (Figure 3b,f) and other VPO catalysts. This result suggests that ethylene was likely produced mainly from the two
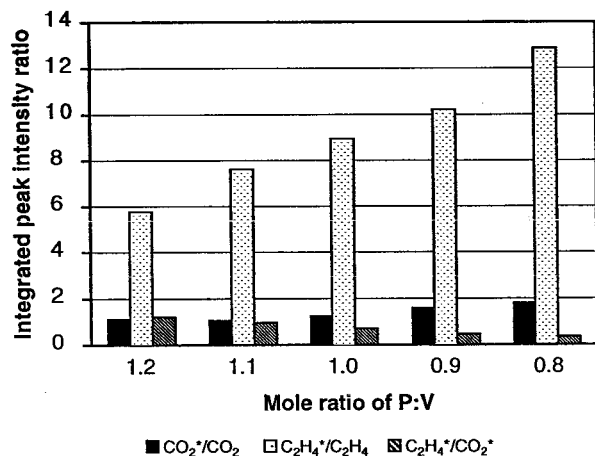
Figure 10. Ratios of the integrated peak intensity of CO_x (sum of CO and CO_2) and ethylene produced from the reaction of either $[1,4\text{-}^{13}C]$butane or fully ^{13}C-labeled butane on the VPO catalysts with different P:V ratios. The reaction temperature was 380 °C. CO_x and C_2H_4 correspond to carbon oxides and ethylene produced from $[1,4\text{-}^{13}C]$butane. $CO_x{}^*$ and $C_2H_4{}^*$ correspond to carbon oxides and ethylene produced from fully ^{13}C-labeled butane.

methylene carbons of *n*-butane, which was not observed in the ^{13}C NMR spectra when $[1,4\text{-}^{13}C]$butane was the reactant.

By further examining the ^{13}C MAS NMR spectra for the oxidation of fully ^{13}C-labeled butane (Figure 9), it was found that the ratio of peak intensity of ethylene to carbon oxides (sum of CO_2 and CO) is close to 1 for P:V = 1.2 and 1.1. This result suggests that there might be a relationship between the formation of ethylene and the formation of carbon oxides on the catalysts with P:V = 1.2 and 1.1. Also, the peak intensity of carbon oxides did not change significantly (fully ^{13}C-labeled butane versus $[1,4\text{-}^{13}C]$butane) for the catalysts with P:V ratios of 1.2 and 1.1 (Figure 10), suggesting that the total oxidation of *n*-butane involves mainly the two methyl groups on these two catalysts.

The combination of these results suggests that the formation of ethylene and carbon oxides might be associated with each other via the following mechanism on the catalysts with P:V ratios of 1.2 and 1.1:

$$*\diagdown\!\!\diagup\!\!\diagdown\!\!\diagup* \xrightarrow{\text{VPO}} CH_2CH_2 + 2\,{}^{13}CO_x \qquad (8)$$
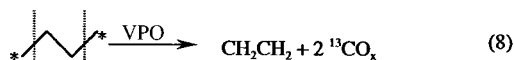
The total oxidation products (CO and CO_2) were formed primarily from the two methyl groups of butane, and the two methylene groups formed ethylene.

The P:V ratio plays a key role in determining the selectivity and activity of the VPO catalysts. Catalysts with P:V slightly greater than 1 had a much higher selectivity and much lower activity than the catalysts with P:V = 1 or P:V < 1 (Figure 11). Our results suggest that the mechanism described in eq 8 might be the major mechanism for the total oxidation of *n*-butane on the more selective VPO catalysts.

Equation 8 is not the only mechanism for the formation of ethylene, because ethylene was always detected in the ^{13}C NMR spectra when $[1,4\text{-}^{13}C]$butane was the reactant. The observed ethylene in the case of $[1,4\text{-}^{13}C]$butane oxidation was likely produced from the following mechanism:

$$*\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown* \xrightarrow{\text{VPO}} 2\,{}^{13}CH_2CH_2 \qquad (9)$$
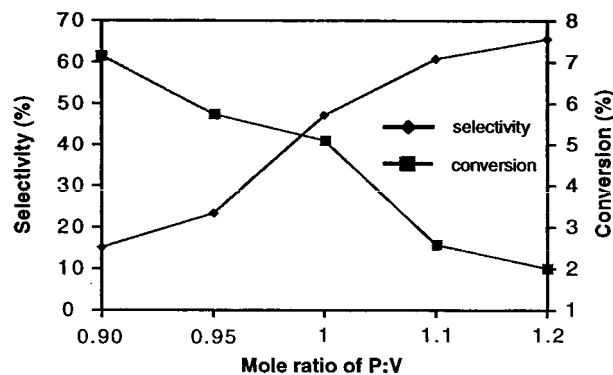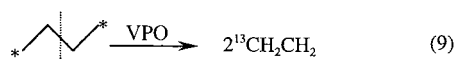
Figure 11. Selectivity to maleic and fumaric acids and conversion of *n*-butane on VPO catalysts with different P:V ratios. The reaction temperature was 380 °C.

The cleavage of the C2−C3 bond of butane resulted in the formation of ethylene from either C1−C2 or C3−C4 of butane. This is the minor mechanism for the formation of ethylene. Ethylene formation by this mechanism might be related to the mechanism of label scrambling, because more ethylene was observed at higher ratios of label scrambling.

Our results also suggest that there is more than one mechanism for the total oxidation of butane, especially on the nonselective catalysts (P:V = 0.90−1.0). Fully ^{13}C-labeled butane yielded more carbon oxides than $[1,4\text{-}^{13}C]$butane on the catalysts with lower P:V ratio (Figure 10), which were also less selective (Figure 11). When P:V = 0.90, which was the least selective catalyst, the peak intensity of carbon oxides almost doubled for fully ^{13}C-labeled butane compared to those for $[1,4\text{-}^{13}C]$butane, indicating that the predominant mechanism for total oxidation of butane on this catalyst was the conversion of the entire butane molecule to carbon oxides:

$$\diagup\!\!\diagdown\!\!\diagup \xrightarrow{\text{nonselective VPO}} 4\,CO_x \qquad (10)$$
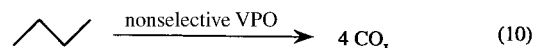
Further evidence is that the ratio of peak intensity of ethylene/CO_x decreased with P:V ratio and dropped to <30% when P:V = 0.9 (Figure 10). This result shows that the contribution to the yield of carbon oxides from the mechanism described in eq 8 decreased with P:V ratio, and correspondingly, the contribution from the mechanism involving the oxidation of all four carbons of butane increased with P:V ratio.

Another explanation that might account for the increase of yield of carbon oxides on the less selective but more active catalysts is the further oxidation of ethylene and maleic acid. Maleic acid and ethylene were reacted at 380 °C on VPO catalysts with P:V ratios of 0.9−1.2 to investigate the possible contributions from these secondary oxidations. Ethylene was almost unreactive on these catalysts at 380 °C (conversion 0−6.2%). A significant amount of maleic acid (20−50%) was oxidized to carbon oxides on the nonselective catalysts. However, for the catalyst with P:V = 0.9, the selectivity to maleic acid was only 15%, which indicates that the oxidation of maleic acid contributes only a small proportion (<10%) to the total yield of carbon oxides, assuming 50% conversion of maleic acid to carbon oxides. Therefore, the 30−90% increase in peak intensity of carbon oxides due to the substitution of fully ^{13}C-labeled butane for $[1,4\text{-}^{13}C]$butane on the catalyst with P:V = 1.0−0.90 can only be attributed to a total oxidation mechanism in which all of the four carbons of butane are
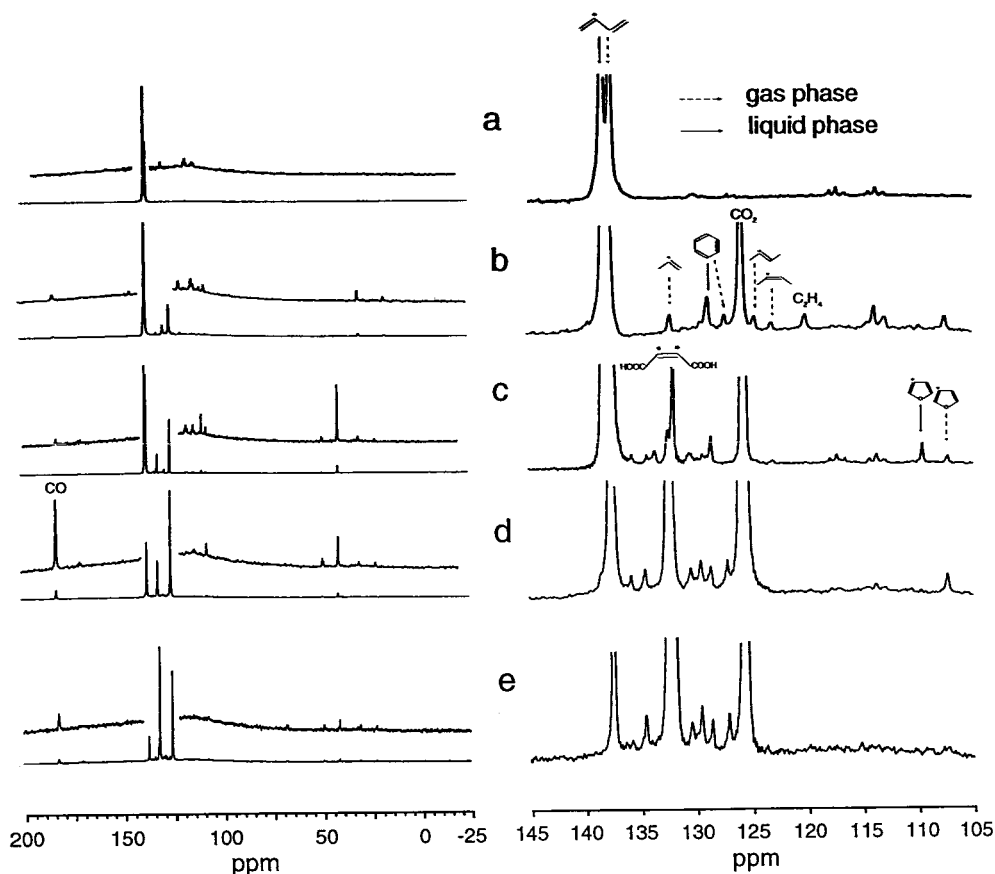
Figure 12. ^{13}C MAS NMR spectra of the reaction products of [2-^{13}C]butadiene on the VPO catalysts with constant P:V ratio (P:V = 1) but different average oxidation state of vanadium: (a) [2-^{13}C]butadiene; (b) VPO3.92 after reaction at 550 °C; (c) VPO4.34 after reaction at 330 °C; (d) VPO4.56 after reaction at 330 °C; (e) VPO4.95 after reaction at 330 °C.

oxidized to carbon oxides, whereas on the catalysts with higher P:V ratios (P:V = 1.2 and 1.1), total oxidation of butane is likely to involve mostly C1 and C4 of butane only.

Reaction of [2-^{13}C]Butadiene on the VPO Catalysts. Butadiene is one of the proposed intermediates for the conversion of *n*-butane to maleic anhydride on VPO catalysts. We have seen that butadiene is unlikely to be a primary reaction intermediate because ~40% label scrambling was observed when *n*-butane reacts on VPO catalysts to form butadiene, whereas typically only 1−7% of the maleic acid was label scrambled. The oxidation of [2-^{13}C]butadiene was performed on some of the VPO catalysts to further compare the reaction behavior of butadiene with *n*-butane. The ^{13}C MAS NMR spectra of the reaction products are shown in Figure 12. No label scrambling in maleic acid was observed for all the catalysts tested. The catalysts showed much higher activity for the oxidation of butadiene compared to that for *n*-butane, especially for the VPO catalysts with higher valence states. Conversion of 20−90% was achieved at 330 °C for butadiene, while for *n*-butane, the conversion was typically less than 1% at this temperature. The selectivity of the oxidation of *n*-butane decreased with increased oxidation state of the VPO catalysts, whereas for butadiene, the selectivity to maleic acid increased with oxidation state of the catalysts. Furthermore, the product distribution for the oxidation of butadiene was quite different from that of *n*-butane. Besides that for maleic acid, many other peaks were also detected for the oxidation of butadiene, though the compounds corresponding to some of these peaks have not

been identified. Only maleic acid and fumaric acid were detected as the major partial oxidation products of butane. Ethylene, methanediol, acetylene, and acetic acid are the byproducts for the oxidation of *n*-butane, but they were not seen in butadiene oxidation. All these results suggest that the mechanisms for the oxidation of *n*-butane and butadiene on VPO catalysts are different and that butadiene is unlikely to be a primary reaction intermediate for the oxidation of *n*-butane to MA.

Summary of Results. Following is the summary of the results obtained using our experimental protocol:

1. Maleic acid, fumaric acid, carbon oxides, ethylene, and methanediol were detected when *n*-butane reacted on VPO catalysts containing V[5+]. Butenes, butadiene, and furan were formed when *n*-butane reacted on the VPO catalysts containing V[4+] and V[3+] only.

2. Label scrambling was observed in the products when [1,4-^{13}C]butane reacted on VPO catalysts. When *n*-butane reacted on the VPO catalysts to produce maleic acid and fumaric acid, the percentage of label scrambled products was ~1−15%, and was typically around 5%. Higher P:V ratios of the catalyst and lower reaction temperatures favored label scrambling. When [1,4-^{13}C]butane reacted on VPO catalysts to form butenes, butadiene, and furan, the percentage of label-scrambled products was around 40%, and this value did not change with P:V ratio and reaction temperature.

3. Ethylene was always a side product for *n*-butane oxidation to maleic acid on VPO catalysts. The peak intensity of ethylene increased by a factor of 5−13 when [1,4-^{13}C]butane was

substituted with fully ^{13}C-labeled butane for the reaction on VPO catalysts containing V[5+]. The yield of ethylene was almost equal to the yield of carbon oxides for the oxidation of fully ^{13}C-labeled butane on VPO catalysts with P:V ratios = 1.2 and 1.1. For the less selective and more active catalysts (P:V =1.0, 0.95, and 0.9), more carbon oxides were produced than ethylene. When [1,4-^{13}C]butane reacted on VPO catalysts to form maleic acid, a larger ethylene peak was usually observed when there was a relatively higher amount of label scrambling.

4. Acetylene was always detected when fully ^{13}C-labeled butane reacted on VPO catalysts to form maleic acid but was almost never detected when [1,4-^{13}C]butane was the reactant.

5. Methanediol was always a byproduct when *n*-butane reacted on VPO catalysts to produce maleic acid. The ^{13}C NMR peak intensity did not change significantly when [1,4-^{13}C]butane was replaced with fully ^{13}C-labeled butane.

6. Butadiene reacted on the VPO catalysts to produce high yields of maleic acid at much lower tempeartures than *n*-butane. No ethylene, methanediol, or label scrambling was observed for butadiene oxidation. On the other hand, many other partial oxidation products were detected. The selectivity and conversion for butadiene oxidation increased with the oxidation state of the catalyst, whereas for *n*-butane, the selectivity and conversion decreased with the oxidation state of the catalyst.

Discussion

Mechanism of Label Scrambling. The most interesting result reported here is that label scrambling occurs in the products when [1,4-^{13}C]butane reacts on the VPO catalysts to produce maleic acid and butadiene. Label scrambling could occur in several different ways! The most intuitive would involve a cyclic intermediate, which suggests that [1,4-^{13}C]butane would produce 1,2-^{13}C, 1,3-^{13}C, or 2,3-^{13}C products. It is unlikely that the label-scrambled products are 1,2-^{13}C compounds since no [13]C–[13]C coupling was observed in the ^{13}C NMR spectra for either maleic acid or butadiene. The label-scrambled products could be either 1,3-^{13}C or 2,3-^{13}C compounds since the [13]C–[13]C coupling for both of them is negligible. It is difficult to envision a mechanism that produces 1,3-^{13}C that does not also produce a significant amount of 1,2-[13]C. We will therefore assume that most of the label-scrambled products are 2,3-[13]C.

Neither of the two representative reaction pathways proposed in the literature, denoted the "olefinic" route and the "alkoxide" route,[18] suggest the possibility or provide a mechanism for label scrambling. In the olefinic route, butane is oxidized to maleic anhydride via butenes, butadiene, and furan sequentially. No cyclic species are proposed which might result in label scrambling. In the alkoxide route, reaction intermediates are bound to the catalyst via either the C–O–V or C–O–P bond[18,19] until desorption as maleic anhydride. Neither of these mechanisms explains the observed label scrambling.

Label scrambling in the products of butane oxidation on VPO catalysts must involve the cleavage of an old C–C bond and the formation of a new C–C bond when label scrambling occurs. C–C bond formation is facile in certain organometallic compounds via many mechanisms such as cyclopropanations, vinylation, metathesis, cross-coupling, etc.[30–32] A common

mechanism for C–C bond formation via organometallic intermediates is reductive elimination:[33]

$$L_nMR_2 \rightarrow L_nM + R-R \qquad (11)$$
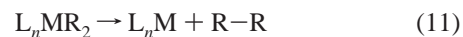
M can be many transition metals, such as Ni, Pd, Au, etc. Sometimes the reductive elimination mechanism results in a ring closure reaction, such as the intramolecular hydrocylation of 4-pentenal catalyzed by Rh(PPh$_3$)$_3$Cl:[34]

$$(M = Rh(PPh_3)_2Cl)$$
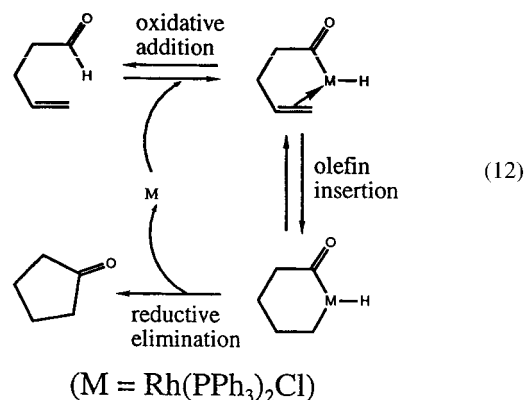
Transition metal complexes act as homogeneous catalysts for these reactions. Little evidence has been reported in the literature that similar mechanisms could operate in heterogeneous catalysis, partially due to the difficulty in detecting organometallic intermediates under heterogeneous catalytic conditions.

As stated previously, it is unlikely that a cyclic intermediate is formed because of the isotopic label distribution. There is, however, evidence that the formation of a four-membered ring might be occurring. When C1 and C4 of the activated butane approach each other during the formation of the new C1–C4 bond, tension along the ringlike structure begins to accumulate. The accumulated tension is distributed along the three C–C bonds in butane: C1–C2, C2–C3, and C3–C4. It is possible that the C2–C3 bond of butane might break before the formation of the C1–C4 bond, or concertedly with the formation of the C1–C4 bond, which results in different products (Scheme 1). If the cleavage of C2–C3 happens first, two ethylene molecules are formed (Scheme 1a). If the cleavage of C2–C3 happens concertedly with the formation of C1–C4, then the observed label scrambling is achieved (Scheme 1b). In either case, no four-membered ring is really formed. This explains why ethylene is always observed as a side product of the reactions and usually more ethylene was observed in the ^{13}C NMR spectra of the reaction products when the ratio of label scrambling was higher.

Mechanism for the Selective Oxidation of Butane on VPO Catalysts. There have been controversies in the literature over whether the olefinic route or the alkoxide route is the dominant mechanism in the conversion of *n*-butane to maleic anhydride.[2,4,18] We have shown that the olefinic route is unlikely to be the dominant reaction pathway due to the inconsistency in the percentage of label-scrambled products when butane reacts on the VPO catalysts to produce butadiene and maleic acid.[24]

(30) Brouwer, D. M.; Hogeveen, H. *Prog. Phys. Org. Chem.* **1972**, *9*, 179–240.
(31) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill Book Co.: New York, 1979; p 23.
(32) Keim, W. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH Press: New York, 1998; Vol. 1, p18.
(33) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons Press: New York, 1994; p 151.
(34) Sakai, K.; Ide, J.; Oda, O.; Nakamura, N. *Tetrahedron Lett.* **1972**, *13*, 1287–1290.

Scheme 1
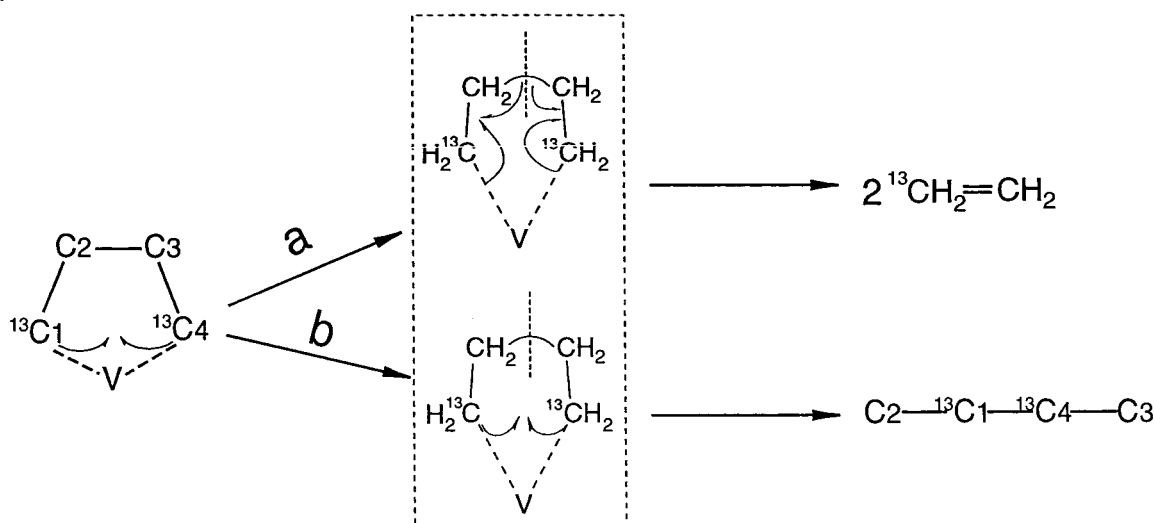
This gives some credence to an alkoxide route, but this mechanism does not explain many of our results.

Here we propose a different mechanism for the selective oxidation of butane based on our results. It is a single-site organometallic mechanism. We want to be extremely clear that we have observed no surface-bound species that would corroborate our results. However, we present this mechanism as an alternative to the alkoxide and olefinic mechanisms that have been previously proposed. This mechanism consists of the following steps:

1. Butane is activated, which involves the cleavage of a methylene carbon–hydrogen bond on the catalyst surface.[20]

2. The activated butane rearranges to coordinate with a vanadium ion via C1 and C4 of butane, forming a chelating configuration as shown in Scheme 2.

3. Label scrambling and the formation of ethylene result from the chelating configuration. It is most likely that label scrambling occurs at the beginning of the formation of the chelating configuration and before the activated butane is further oxidized, as illustrated in Scheme 2a,b.

4. If there is enough V^{5+} in the catalyst, the activated butane will be further oxidized by the lattice oxygen while it remains in the chelating configuration until it is desorbed as maleic anhydride. This is a single-site reaction, which means the reaction intermediates do not move to other sites during the reaction. However, the oxidation of butane to maleic anhydride involves the insertion of 3 oxygen atoms, abstraction of 8 hydrogen atoms, and transfer of 14 electrons. These steps are achieved on a single site by the theory proposed by Weiss et al.[35] for the catalytic oxidation of hydrocarbons on metal oxide catalysts, though it was originally proposed for the reaction of unsaturated hydrocarbons. The theory can be represented by Scheme 3, where S_R represents the substrate to be oxidized and S_O stands for the oxidation product. S_R is adsorbed on a site M_1 having the character of an electron acceptor, generally the cation with the highest valences.[35] Oxidation of the substrate occurs on this site. Lattice oxygen atoms are transferred to this site to complete the oxidation. The electrons produced by the reaction are transferred to another site, M_n, which undergoes
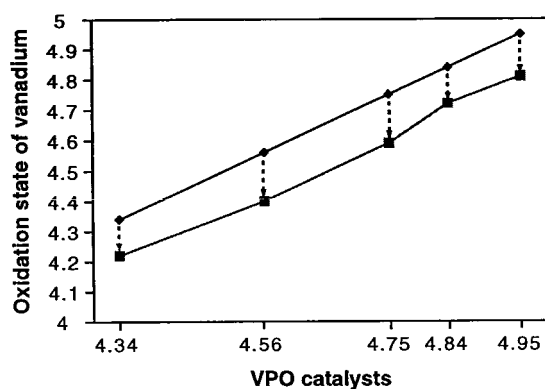

Figure 13. Changes in the average oxidation state of vanadium in the VPO catalysts after reaction with [1,4-^{13}C]butane at 380 °C.

reduction and becomes an electron-donor site, on which molecular oxygen can be adsorbed for the reoxidation of the system. This is actually a detailed description of the Mars and Van Krevelen mechanism.[36] Because there is no molecular oxygen in our pseudo-flow reaction system, the above scheme needs to be modified: there is no reoxidation of the catalyst but just flow of electrons and oxygen atoms within the catalyst. Evidence has been reported in the literature that all oxygen and hydrogen atoms in the surface layer of VPO catalysts are in fast exchange relative to the time scale of the conversion of butane to maleic anhydride.[20] This supports the single-site mechanism in that enough oxygen can be transported to the reaction site during butane oxidation. Our experiments also showed that the catalysts were significantly reduced after the reaction (Figure 13), indicating that not only the surface oxygen, but also oxygen in the bulk structure of the catalyst, is available to the reaction. The single-site mechanism also explains why no intermediate products can be detected when there is sufficient available oxygen for the oxidation of butane on VPO catalysts,[2] since there is no desorption of the reaction intermediates until maleic anhydride is formed under such reaction conditions.

5. The peak intensities of CO_x and ethylene are almost equal when fully ^{13}C-labeled butane reacts on the selective VPO catalysts (Figures 9 and 10), which indicates that the formations of CO_x and ethylene are associated with each other. We suggest
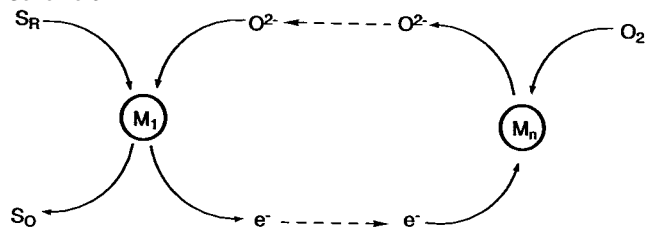
(35) Weiss, F.; Marion, J.; Metzger, J.; Cogion, J.-M. *Kinet. Catal. (Engl. Transl.)* **1973**, *14*, 32–53.

(36) Mars, P.; Van Krevelen, D. W. *Chem. Eng. Sci.* **1954**, *3*, 41–59.

Scheme 2
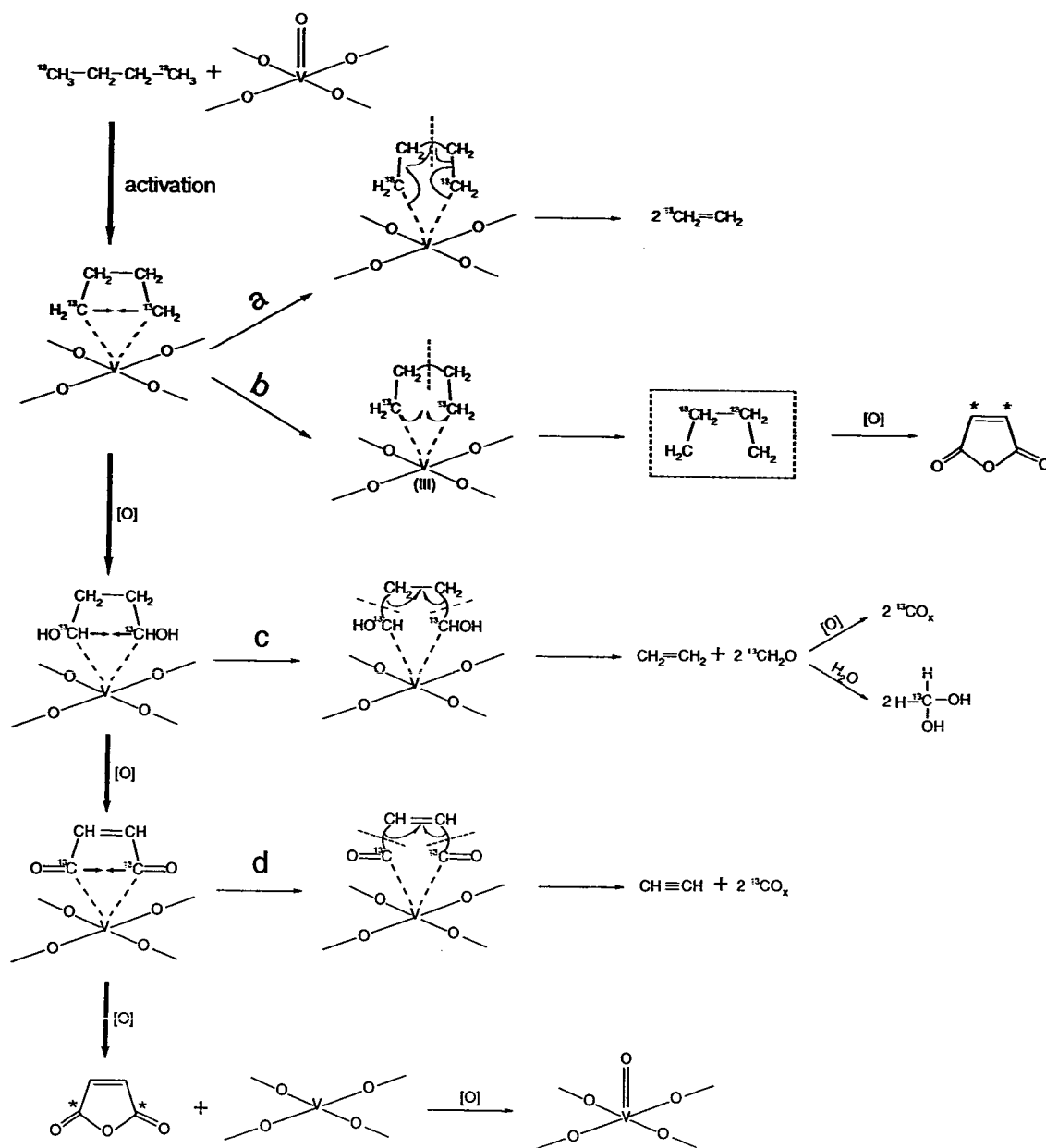
Scheme 3

that this is also the result of the chelating configuration. Oxygen insertion on C1 and C4 might be the next step after butane has been activated (Scheme 2c). The tendency still exists for C1 and C4 to form a C—C bond after oxygen insertion has occurred, because the molecule still maintains the chelating configuration. However, at this point the insertion of oxygen on C1 and C4 of butane weakens the C1—C2 and C3—C4 bonds. Therefore, when C1 and C4 approach each other, the C1—C2 and C3—C4 bonds are easier to break than the C2—C3 bond, which results in the
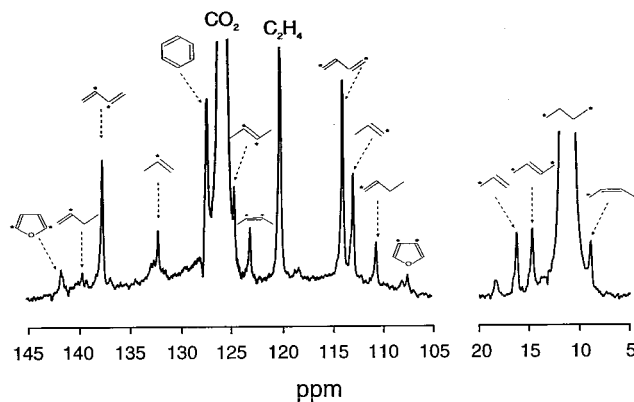

Figure 14. Label scrambling in butenes, butadiene, and furan when [1,4-^{13}C]butane was reacted on VPO catalyst with P:V = 0.95 at 550 °C.

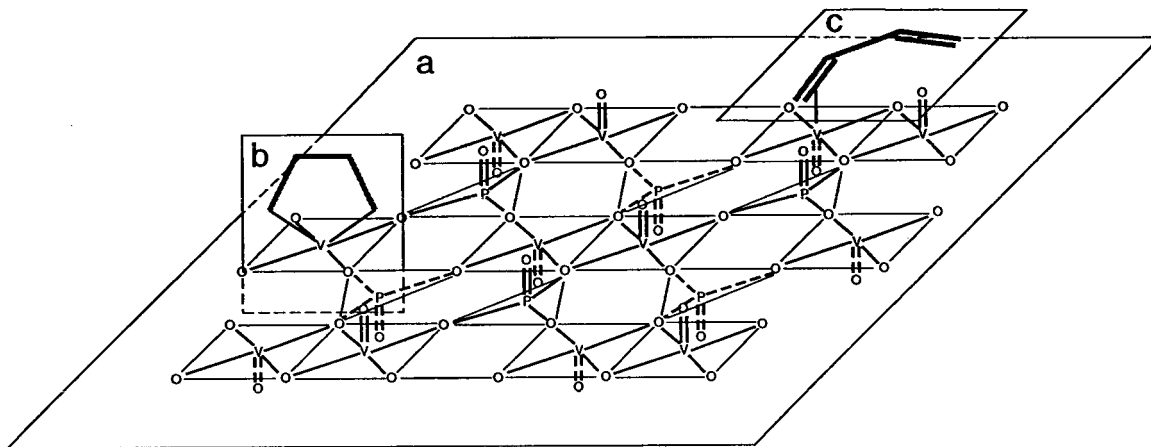formation of an ethylene molecule consisting of C2 and C3, and two formaldehyde or methanediol molecules (Scheme 2c).

Figure 15. Proposed scheme for the interaction of *n*-butane and butadiene with the surface of the VPO catalyst. (a) Idealized vanadyl pyrophosphate structure.[2] (b) Activated *n*-butane in the chelating configuration, molecule forming a σ-complex with the vanadium ion. (c) Butadiene forms π-complex with the vanadium ion on the surface of the catalyst.

The methanediol peak is always observed for the reaction of butane on VPO catalysts containing V^{5+} and can be exceptionally high under certain circumstances (Figure 10). Formaldehyde was not detected since formaldehyde exists completely as its hydrate (methanediol) in aqueous solution.[37] This gives the second mechanism and the main mechanism for the formation of ethylene, because the peak intensity of ethylene increased by a factor of 5−13 when 1,4-^{13}C-labeled butane was substituted by fully ^{13}C-labeled butane. Methanediol is not a stable compound under the reaction conditions. Most of it will be further oxidized to CO or CO_2. Because the ratio of the peak intensity of ethylene/CO_x is close to 1:1 on the more selective catalysts (Figure 9), it is likely that total oxidation of butane on these catalysts involves mainly the oxidation and abstraction of C1 and C4 of butane, and ethylene is the remaining part of butane (C2 and C3) after C1 and C4 have been oxidatively removed. It is likely that formation of acetylene also occurs by a similar mechanism. When butane is further oxidized so that the two methylene groups have become methine groups (Scheme 2d), the cleavage of the C1−C2 and C3−C4 bonds will result in the formation of acetylene from C2 and C3 of butane. Therefore, acetylene is unlikely to be detected in the ^{13}C NMR spectra of the reaction products using [1,4-^{13}C]butane but was always detected when fully ^{13}C-labeled butane was used.

6. Under oxygen-lean conditions (no gaseous oxygen or no V^{5+} in the catalyst), the catalyst is unable to oxidize butane to maleic anhydride,[15,16] and the reaction intermediates may desorb as butenes, butadiene, and furan. The ratios of products containing 1,4-^{13}C to 2,3-^{13}C for butenes, butadiene, and furan were almost identical (Figure 14), suggesting that label scrambling occurs at the first step of butane oxidation: butane → butenes. The observed label scrambling in butadiene and furan is likely to result from the subsequent oxidation of label-scrambled butenes. The same chelating configuration mechanism as that shown in Scheme 2 is proposed to be responsible for label scrambling of these compounds. The large amount of ethylene observed in the ^{13}C NMR spectra of the reaction products when [1,4-^{13}C]butane reacted on the VPO catalysts to produce butenes, butadiene, and furan (Figure 4) further

indicates the relationship between the formation of ethylene and label scrambling as shown in Scheme 2a,b.

Differences between the Oxidations of *n*-Butane and Butadiene on VPO Catalysts. The proposed mechanism for the selective oxidation of butane on VPO catalysts is unlikely to be applicable to butadiene due to the differences in their reaction behavior. It has been suggested the active phases for the selective oxidation of butane and 1-butene are $(VO_2)_2P_2O_7$ and β-$VOPO_4$, respectively, and different mechanisms operate for the oxidations of butane and 1-butene.[38] On the basis of current results, different mechanisms for the interactions of butane and butadiene with VPO catalysts are proposed (Figure 15). The activated butane is adsorbed on the surface of the catalyst via a chelating configuration (σ-complex, Figure 15b), whereas butadiene forms a π-complex with V^{5+}, which does not need as high a temperature to form as that needed for the activation of butane (Figure 15c). The activation of butane involves the cleavage of a C−H bond, which apparently has a much higher activation energy than that for the formation of a π-complex and needs a much higher temperature for the reaction to occur. The chelating configuration of butane results in label scrambling and formation of ethylene, which are unlikely to be produced by the π-complex when butadiene interacts with the catalyst. The chelating configuration ensures that the reaction intermediates do not move to other sites during the oxidation until maleic anhydride is formed, which explains why no other partial oxidation products are detected for butane oxidation. The π-complex is likely to be much more flexible and mobile on the surface of the catalyst. When one end of the molecule (butadiene or butenes) forms a π-complex with a vanadium ion, the other end of the molecule may interact with different sites on the catalyst, which might be the reason various partial oxidation products can be formed. The relative ease for the formation of π-complexes means the catalyst may lose its activity quickly if there are only a few V^{5+} sites on the surface of the catalyst due to the strong absorption of olefinic species on the surface of the catalyst.[2] Therefore, a higher oxidation state of the catalyst favors the oxidation of butenes or butadiene. On the other hand, selective oxidation of *n*-butane requires V^{5+} to be isolated on the surface of the catalyst, so that once butane

(37) Ternay, A. L. *Contemporary Organic Chemistry*; W. B. Saunders Co.: Philadelphia, 1979; p 682.

(38) Bordes, E. *Catal. Today* **1993**, *16*, 27−38.

is activated by a V^{5+}, it forms the chelating configuration in situ with the specific vanadium ion, and is further oxidized to maleic anhydride via the single-site organometallic mechanism. The activated butane can be oxidized to carbon oxides by the surrounding V^{5+} sites before the chelating configuration is formed. Therefore, the oxidation state for the VPO catalysts of best performance was found to be within 4.00−4.03,[2,3,39] at which V^{5+} is well isolated on the surface of the catalyst, or in other words, V^{5+} sites exist as $VOPO_4$ islands on a $(VO_2)_2P_2O_7$ matrix to minimize the total oxidation, as described by Centi.[3]

Summary

A single-site organometallic mechanism is proposed for the selective oxidation of *n*-butane on VPO catalysts based on ^{13}C NMR studies of the reaction. The activited butane is proposed to form a chelating configuration on the surface of the catalyst via the coordination of C1 and C4 of butane with the vanadium ion. The chelating configuration is maintained during the reaction until the formation of maleic anhydride. Label scrambling, the formation of ethylene, and other observations are explained using this reaction model. Butadiene is proposed to form π-complexes with the catalyst.

JA010285V

(39) Albonetti, S.; Cavani, F.; Trifirò, F. *Catal. Rev.-Sci., Eng.* **1996**, *38*, 413−438.