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A molecular level mechanism of *n*-butane oxidation to maleic anhydride over vanadyl pyrophosphate

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A molecular level mechanism is proposed for the highly selective 14-e^- oxidative transformation of *n*-butane to maleic anhydride on the surface of vanadyl pyrophosphate. The mechanism suggests that the dimeric active sites assume at any given time, one of four possible interconvertible states which differ from each other in the number of available oxygen atoms and the formal oxidation states of the individual vanadium atoms. The relative ratios of active sites in each of the four possible states are dictated by the reaction conditions, the redox properties of the reacting gases and the structure of the vanadyl pyrophosphate active surface. A crucial feature of the mechanism is a "pseudo-ozonide" surface species formed by the interaction of a chemisorbed dioxygen molecule and an adjacent metal-oxo group. This unusual species is responsible for the initial activation of the *n*-butane, which occurs when the chemisorbed dioxygen abstracts an H-atom from the alkane and the adjacent metal-oxo group reacts with the incipient alkyl radical to form an alkoxy group. The proposed mechanism is entirely consistent with literature reports describing the behaviour of $(VO)_2P_2O_7$ in flow, pulse and TAP reactors.

Keywords: Selective oxidation; *n*-butane; maleic anhydride; $(VO)_2P_2O_7$; mechanism; site isolation

1. Introduction

Over the past two decades, intensive studies in both academic and industrial laboratories have shed considerable light on the title reaction and the nature of the catalyst performing this remarkably selective, 14-electron oxidative transformation of *n*-butane to maleic anhydride [1,2]. There are several hypothetical mechanistic schemes that have been proposed to describe this system at the molecular level [3,4], however, they differ considerably from each other and no comprehensive scheme has yet been formulated that would describe the surface state dynamics of the catalyst during the complete redox reaction cycle, as has been done in great detail for the propylene oxidation and ammoxidation on Bi-molybdates and Fe- or U-antimonates [5].

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Recently, Thompson and Ebner [6] reexamined the crystal structure of the active phase, $(VO)_2P_2O_7$, of these highly selective paraffin oxidation catalysts and postulated a detailed "zeroth-order" model of the topology of the catalytically active surface, which is formed by terminating the crystal parallel to the (100) plane [7]. The "site-isolation" principle, first proposed by Grasselli and Callahan [8], which requires that the active oxygen on the surface of the selective catalyst be present in isolated regions, is one of the key features of their model. Although it is clear that subsurface, i.e. lattice, oxygen does not play a dominant role in this reaction, the exact chemical form of the active oxygen involved in the reaction is still uncertain [9].

Based on an analysis of the electronic structure of the vanadyl pyrophosphate surface using extended Hückel calculations, Schiøtt et al. [10] suggested that 1,3-butadiene, assumed to form from *n*-butane by some mechanism involving the initial abstraction of a methylene hydrogen [11], undergoes a [4 + 2]-like concerted cycloaddition reaction with an oxygen atom of a vanadyl group on the surface, and the thus formed adsorbed 2,5-dihydrofuran species is transformed to maleic anhydride by reaction with molecular dioxygen adsorbed on the adjacent Lewis acidic vanadium atom.

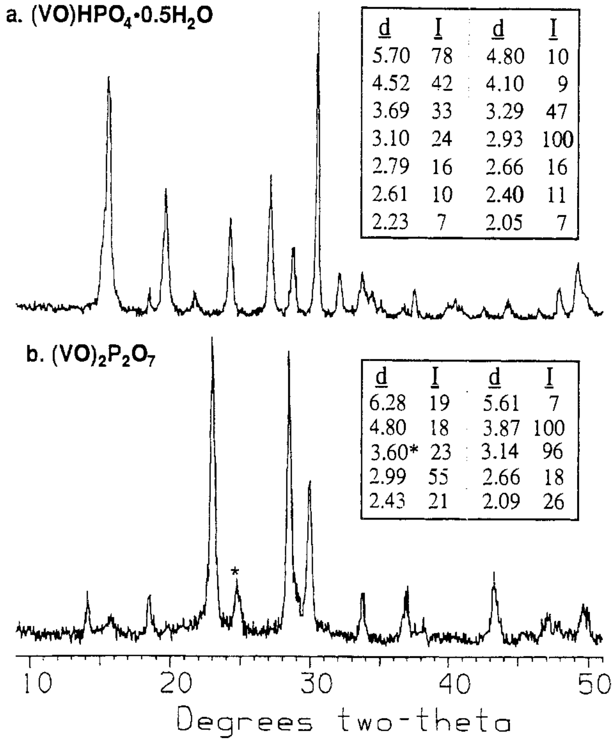
We report now some experimental results supporting a key feature of this incomplete mechanism, viz. that molecular dioxygen is an obligatory oxidant in the highly selective transformation of *n*-butane to maleic anhydride on the surface of the vanadyl pyrophosphate catalyst. However, the main thrust of our paper is a proposed detailed molecular level mechanism, which describes step-by-step, the surface dynamics involving redox transformations of the active sites during the 14-electron oxidation of *n*-butane to maleic anhydride. This newly proposed mechanism can be used to explain a large number of experimental observations reported to date on this system.

2. Experimental

2.1. CATALYST SYNTHESIS

Preparation of $VO(HPO_4)\cdot\frac{1}{2}H_2O$ [12]. V_2O_5 (100 g, 0.55 mol) was refluxed in isobutanol (1 ℓ) for 20 h. Tetraethoxysilane (122 g, 0.59 mol) was then added followed by phosphoric acid (85% w/w, 150 g, 1.30 mol). The mixture was then stirred and refluxed for 14 h and allowed to cool. The light blue precipitate was collected by filtration through a medium pore glass frit. The XRD pattern, fig. 1, showed that this was the precursor phase $VO(HPO_4)\cdot\frac{1}{2}H_2O$. The surface area, determined by N_2 BET measurements, was found to be ~ 24 m^2 g^{-1}.

Preparation of 50% V_2O_5/SiO_2. NH_4VO_3 (7.7 g) was mixed with $H_2C_2O_4\cdot 2H_2O$ and 140 ml distilled H_2O. The slurry was stirred and heated until a clear red-brown solution was obtained. LUDOX-AS 40 (15 g) was then added and



d	I	d	I
5.70	78	4.80	10
4.52	42	4.10	9
3.69	33	3.29	47
3.10	24	2.93	100
2.79	16	2.66	16
2.61	10	2.40	11
2.23	7	2.05	7

d	I	d	I
6.28	19	5.61	7
4.80	18	3.87	100
3.60*	23	3.14	96
2.99	55	2.66	18
2.43	21	2.09	26

Fig. 1. XRD-patterns (Cu Kα radiation) of (a) the precursor phase $(VO)HPO_4 \cdot \frac{1}{2}H_2O$ and (b) the catalytically active phase $(VO)_2P_2O_7$, generated in situ by heating the precursor phase at 400°C, in a flow of air containing ~ 1.5% *n*-butane. The peak marked with an asterix is due to quartz packing in the reactor above and below the catalyst bed.

the mixture evaporated to dryness. The residue was ground and heated in a quartz crucible at 450°C for 10 h. The red-brown powder was used without any further treatment. The surface area, determined by N_2 BET measurements, was found to be ~ 53 $m^2 g^{-1}$.

Preparation of 10% $CoMoO_4/TiO_2$ [13]. $(NH_4)_6Mo_7O_{24} \cdot H_2O$ (2.65 g) was mixed with $Ti_2(C_2O_4)_3 \cdot 10H_2O$, oxalic acid (5 g) and water (200 ml). The slurry was stirred and evaporated to dryness. The residue was then ground and heated at 500°C for 10 h. A solution of $Co(NO_3)_2 \cdot 6H_2O$ (1.05 g) and $(NH_4)_6Mo_7O_{24} \cdot H_2O$ (0.65 g) in 25 ml of water was then added and the mixture evaporated to dryness. The residue was ground and heated to 550°C for 3 h. The light purple product was used without any further treatment. The surface area, determined by N_2 BET measurements, was found to be ~ 24 $m^2 g^{-1}$.

2.2. REACTION APPARATUS

The catalysts prepared as described above were evaluated in a standard fixedbed microreactor unit. The analysis of the product stream was performed using an on-line Varian model 3600 GC and a Carle refinery gas analyser. The product stream was maintained at $>220°C$ until it had passed through the sampling loop of the Varian GC. A large diameter (6.0 cm) air-cooled trap in-line immediately after the Varian GC was found to be an effective way of avoiding the clogging of the system by the solid maleic anhydride.

2.3. DATA ANALYSIS

The composition of the feed was adjusted to approximate 1.5% n-C_4 in air, which is below the lower explosion limit for this mixture. The conversions are defined as the molar percentage of each reactant in the feed that is converted to products. The yields of carbon containing products are defined as the percentage of carbon in the butane converted that is present in each of these products. The selectivity to each product is defined as the ratio of the yield of that product divided by butane conversion. The carbon, hydrogen, oxygen and nitrogen balances were $100 \pm 5\%$ and all results were normalized assuming no loss of carbon. Blank runs conducted over acid-washed quartz chips under conditions similar to the actual experimental runs showed no reaction. Blank runs were also conducted to establish that nitrous oxide is not decomposed over any of the catalysts in the temperature range 400–500°C.

3. Results

The precursor phase prepared as described above was pelleted to 20–40 mesh size, loaded in the quartz microreactor and converted to the active phase, vanadyl pyrophosphate, in situ by heating to 400°C with the feed gas consisting of $\sim$ 1.5% n-butane in a $\sim$ 20/80 mixture of oxygen and nitrogen flowing over it at a rate of $\sim$ 100 ml min^{-1}. The X-ray powder diffraction patterns (Cu Kα radiation) of the precursor phase and the equilibrated catalyst unloaded from the reactor after the catalytic experiments are shown in fig. 1. The catalyst bed volume was $\sim$ 2.6 ml, thus giving a contact time of $\sim$ 1.5 s. The only products observed were maleic anhydride and carbon oxides. The stability of the catalyst was monitored during the course of the experiments described below by periodically returning to these initial conditions and determining the n-butane conversion and the product distribution. After the catalyst had equilibrated about 80 h on stream, the feed gas composition was changed to $\sim$ 1.5% n-butane in a 40 : 60 v/v mixture of N_2O and N_2, and the product stream analyzed as described above. The feed gas composition was then switched back to the original composition and the products again analyzed to confirm that the catalyst was still active under the normal operating conditions. This complete set of experiments was also conducted at 450°C and similar experiments were also performed under comparable conditions after changing the catalyst to (i)

50% V_2O_5/SiO_2 and (ii) 10% $CoMoO_4/TiO_2$. The latter is one of the few catalysts for maleic anhydride synthesis from *n*-butane that does not contain vanadium [13]. The *n*-butane conversions over the three catalysts when molecular oxygen is the oxidant are plotted together in fig. 2, while fig. 3 shows a plot of the conversions observed when nitrous oxide is the oxidant.

4. Discussion

The active surface of vanadyl pyrophosphate consists of dimeric units formed by edge-sharing between two square-pyramidal VO_5 groups, with the apical oxygen atoms of the two groups pointing in opposite directions, so that on the surface, each dimeric unit has one metal-oxo group adjacent to a strong Lewis acid site. These active sites are linked together by phosphorus atoms to form layers that in turn are linked together by P–O–P linkages to form the three-dimensional structure of $(VO)_2P_2O_7$. The layers are aligned so that the vanadyl groups form pairs of V=O- -V=O chains pointing in opposite directions perpendicular to the surface. The dimeric active sites form clusters on the surface, composed each of four vanadium dimers, that are isolated from each other by excess phosphorus, present in the form of pyrophosphate groups, as shown schematically in fig. 4. These pyrophosphate groups serve as diffusion barriers, preventing excess oxygen from neighbour-

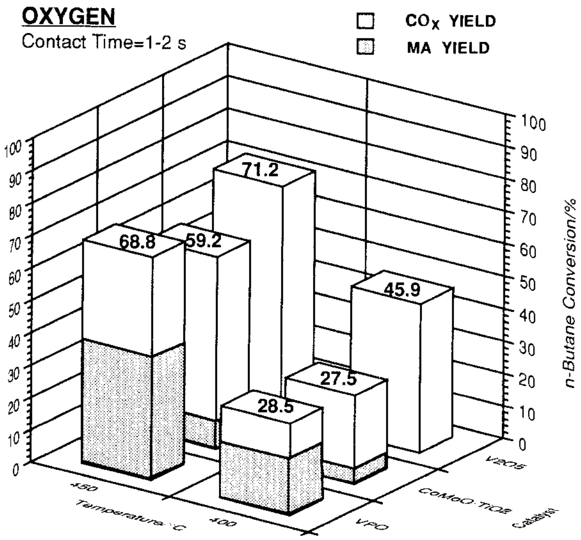


Fig. 2. Conversion of *n*-butane over three different catalysts at 400 and 450°C and contact times of ~ 1–2 s, with molecular oxygen as the oxidant. The conversion levels are similar over all three catalysts but the selectivities to maleic anhydride are vastly different. Over $(VO)_2P_2O_7$, the selectivity to maleic anhydride is around 55–65% while it is zero over 50% V_2O_5/SiO_2 and 14–16% over 10% $CoMoO_4/TiO_2$.

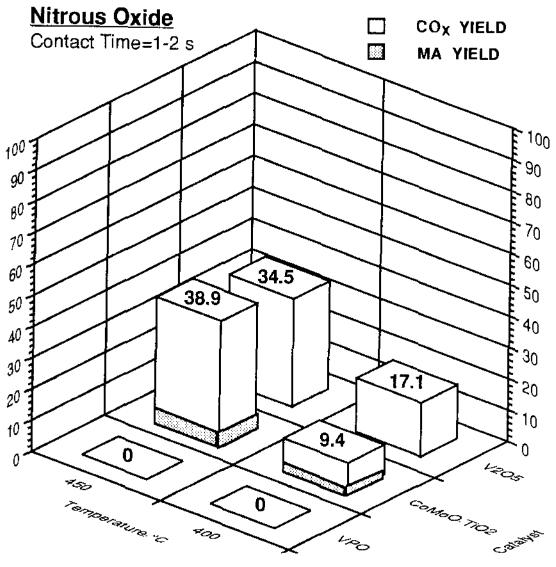


Fig. 3. Conversion of *n*-butane over three different catalysts at 400 and 450°C and contact times of $\sim$ 1–2 s, with nitrous oxide as the oxidant. The conversion levels over 50% V_2O_5/SiO_2 and 10% $CoMoO_4/TiO_2$ are about half to a third of those observed when the oxidant is dioxygen. However, over $(VO)_2P_2O_7$, the *n*-butane conversion is essentially zero. This difference in behavior between oxides in which bulk diffusion of lattice oxygen is possible and $(VO)_2P_2O_7$ in which such diffusion is not possible, is consistent with our hypothesis that molecular oxygen is intimately involved in the activation of *n*-butane at low temperatures over the commercially used catalyst, $(VO)_2P_2O_7$.

ing clusters reaching the reactive surface bound intermediates and thus help prevent overoxidation [14]. They are also Brønsted acid sites and participate in the overall reaction, as described below.

The mechanism we propose for the selective oxidative transformation of *n*-butane to maleic anhydride on the (100) face of the $(VO)_2P_2O_7$ crystallites, suggests that each of the four dimeric active sites per geometrically isolated surface cluster can assume the four distinct states S_0, S_1, S_2 and S_3 described below. The clusters of four active sites are diffusionally isolated from the rest of the surface by the pyrophosphate groups, as described above, and chemisorbed oxygen can hop from site to site within each cluster, possibly aided by an intervening phosphate group, transforming the state of the active sites involved.

We denote the virginal state of the active site by S_1, since it has one available oxygen atom associated with it. When a molecule of dioxygen is adsorbed on the Lewis acid site, the active site is transformed to a state denoted by S_3. This chemisorbed dioxygen could either be a superoxo or a peroxo species [15], however, even though extended Hückel calculations favour the peroxo form by $\sim$ 0.5 eV [10], the superoxo species might still be the predominant form if it is stabilized to some extent by interaction with the adjacent metal-oxo atom. Two additional possible states that

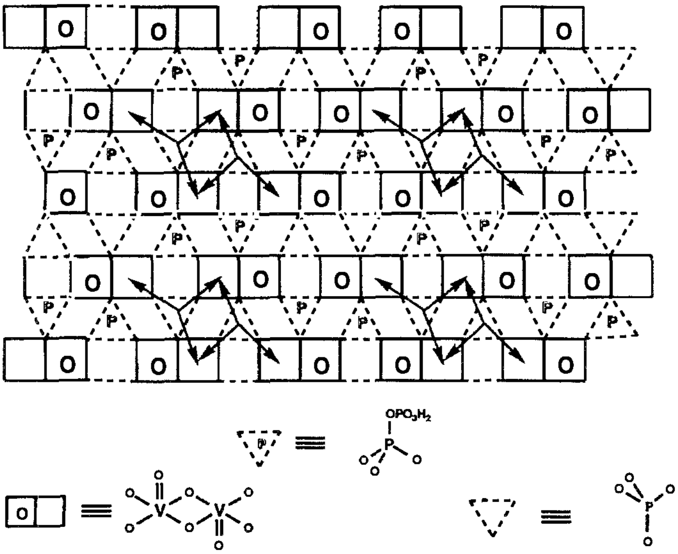


Fig. 4. Schematic representation of the surface structure of one polytype of $(VO)_2P_2O_7$ [16]. The arrows represent the possible pathways for facile exchange of surface bound oxygen, either monoatomic or diatomic, between the active sites. The "site-isolation" due to the diffusion barrier posed by the pyrophosphate groups is clearly shown by these arrows.

the active sites can assume, are denoted by S_0 and S_2, with zero and two oxygen atoms respectively. The structure of the active site in each of these four states is shown in fig. 5, with formal oxidation numbers assigned to each vanadium atom.

Further, according to our proposed mechanism, the initial activation of the *n*-butane is accomplished by hydrogen abstraction from one of the methylene groups of *n*-butane by a superoxo species to give a surface bound hydroperoxy group, and simultaneously the capture of the alkyl radical by the adjacent vanadyl group to give a surface bound alkoxy group. The hydroperoxy group can then rapidly abstract another hydrogen, from either the same methylene group or from one of the adjacent $-CH_x$ groups, to generate a molecule of water and a metal bound ketaloxy or glycoloxy group respectively, as shown in fig. 6. The surface species formed as a result of this step can also be considered to be 2-butanone and 1- or 2-butene, strongly adsorbed on the active site in state S_1 or S_2 respectively. In a TAP reactor [16], due to the extremely low pressure conditions, the butenes can desorb and exit the catalyst bed without undergoing further reaction and therefore be observed as the primary product [9]. Under normal operating conditions, however, the butenes do not desorb as observable intermediates, staying on the surface to react further.

The mechanism we propose suggests that the next step in the sequence of reactions leading to maleic anhydride formation involves the participation of a Brønsted acid site. There is considerable evidence to support this idea, e.g. Aguero

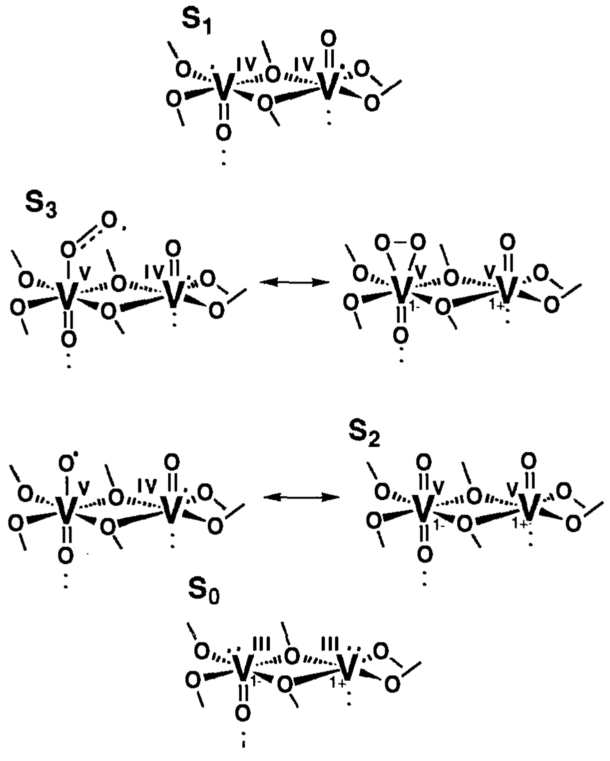


Fig. 5. Schematic representations of the structure of the dimeric active site in the various dynamic states that it can assume during the course of the reaction of *n*-butane with molecular oxygen to form maleic anhydride. In S_3 and S_2 the dimeric active site may undergo one- or two-electron oxidation by the adsorbed dioxygen or atomic oxygen. We propose a one-electron oxidation in state S_3 and a two-electron oxidation in state S_2.

et al. [17] observed that neopentane, which has only three contiguous carbon atoms in the chain, can be converted to maleic anhydride in high yields, a result that can be explained on the basis of the participation of Brønsted acid sites in the mechanism of the reaction. In addition, Centi et al. [18] reported recently that doping the surface of active vanadyl pyrophosphate catalyst with potassium selectively removes the Brønsted acid sites while leaving the Lewis acid sites unaffected. This K-doped catalyst is unable to convert *n*-butane to maleic anhydride, however, it can activate *n*-butane and generate surface bound species of unknown structure, which are slowly oxidized to CO_x in the presence of gaseous oxygen. According to the mechanism we propose these surface bound species are mainly intermediates such as butenes and butanones which, on an undoped catalyst surface, can all be converted to 1,3-butadiene and one molecule of water by acid catalyzed reactions [19], as shown in fig. 7. Thus though there are several alternate intermediates possible in the early stages of the reaction of *n*-butane, as described above, the observed selectivity towards the final product, maleic anhydride, is very

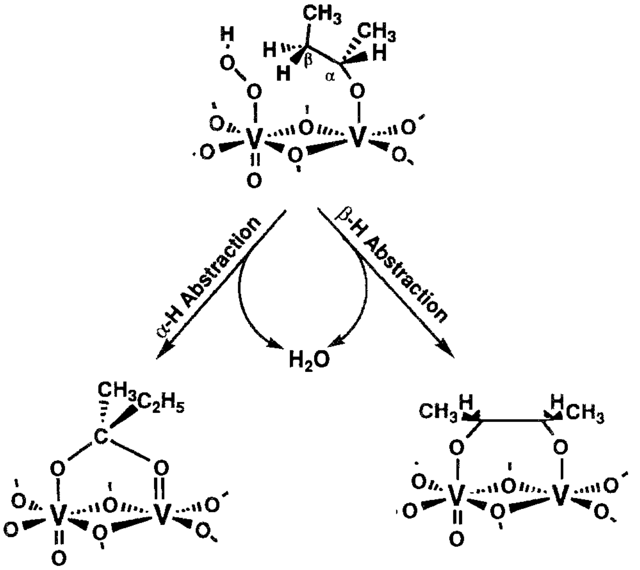


Fig. 6. Surface species generated by the reaction of *n*-butane with the active site in state S_3. The initial activation of the *n*-butane occurs by hydrogen abstraction from a methylene group to give a surface bound hydroperoxy group. The adjacent vanadyl group simultaneously captures the alkyl radical to form a surface bound alkoxy group. The hydroperoxy group can abstract a hydrogen, either α or β, from the alkoxy group to generate water and either of the two surface bound species shown above. These can be seen to be respectively, 2-butanone chemisorbed on the active site in state S_1, or 2-butene chemisorbed on the active site in state S_2.

high. As a result of the acid catalyzed step, 1,3-butadiene is produced and the active site returns to state S_1. Again in a TAP reactor, 1,3-butadiene is able to desorb and exit the catalyst bed, and is observed as the secondary product. The course of the reaction beyond this point has been considered and described in detail on the basis of extended Hückel calculations [20].

At the end of this sequence of elementary reactions, when maleic anhydride is desorbed from the surface, the active site is in state S_0. In this state it can react with dioxygen to from state S_2 or it could also accept an oxygen atom from an adjacent site in state S_2 to form state S_1. If there are two adjacent sites in state S_2, transfer of oxygen atom from one to the other leads to the formation of one site in state S_1 and one site in state S_3. The pathways for the interconversion of the various states of each active site and the substrate reactions that accompany them are shown in fig. 8a. A minimum of three active sites is needed to complete the transformation of *n*-butane to maleic anhydride in the absence of gaseous oxygen [21], however, a fourth site is needed in order to regenerate the original state of the catalyst. A simple model of the surface dynamics [22] of vanadyl pyrophosphate can be written in terms of the proposed isolated cluster of four active sites, and is given in fig. 8b.

The mechanism suggests that oxidants which can provide only one oxygen

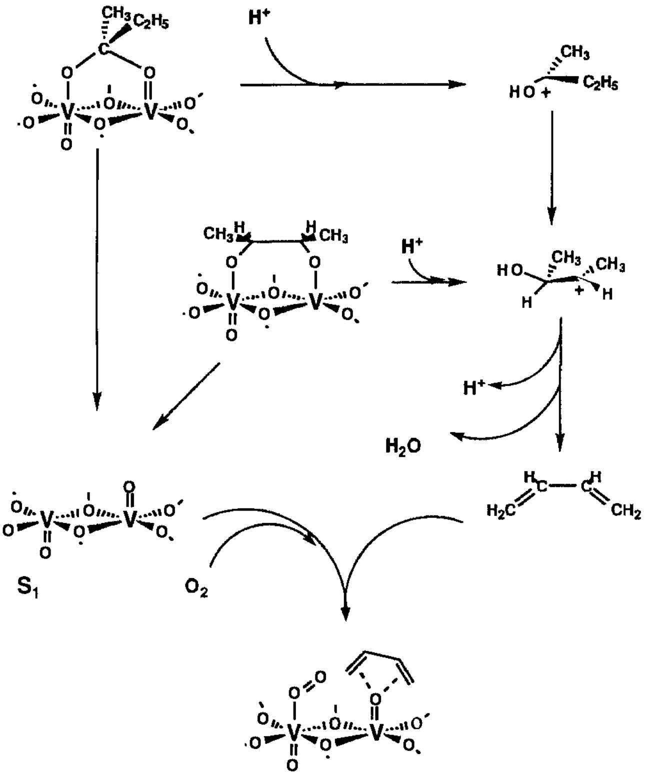


Fig. 7. Acid catalyzed conversion of partially oxidized surface bound intermediates to 1,3-butadiene. The active site is first converted to state S_1 which is capable therefore of adsorbing a molecule of dioxygen and therefore is converted to state S_3. The 1,3-butadiene formed stays strongly adsorbed on the active site by interacting with the oxygen of the vanadyl group and undergoes further reaction to yield maleic anhydride.

atom at a time to the active site, would not be good alkane oxidants over vanadyl pyrophosphate. Thus, nitrous oxide would form structures similar to S_2 which are much less reactive than S_3, the surface state derived directly by the interaction of gaseous dioxygen with the surface. However, the difference in the reactivity of dioxygen and nitrous oxide with alkanes over other metal oxides in which subsurface bulk oxygen is also available for reaction would not be as great as in $(VO)_2P_2O_7$, since in the former an oxygen depleted i.e. reduced, active site is readily replenished with oxygen from the bulk and not necessarily from the gas phase [5].

Our results, which are summarized in figs. 2 and 3, are consistent with the mechanism we propose. In fig. 2, it is seen that under comparable conditions, *n*-butane is converted to approximately the same extent by all three catalysts investigated, albeit with vastly different selectivity to maleic anhydride, when molecular oxygen is the oxidant. In contrast, fig. 3 shows that when nitrous oxide is the oxidant, *n*-butane conversion drops to $<1\%$ over the vanadyl pyrophosphate catalyst

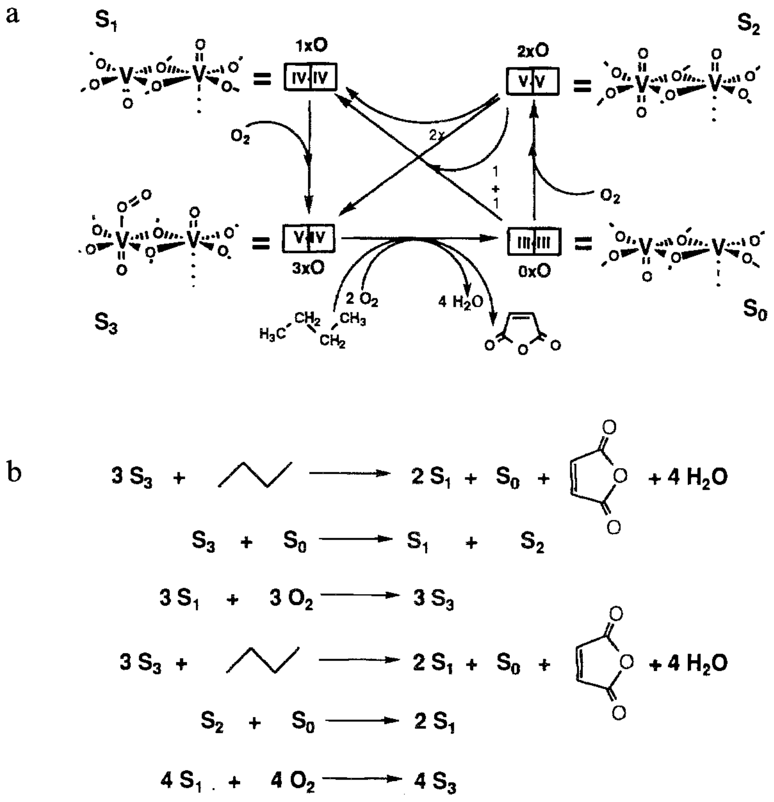


Fig. 8. (a) Transformation pathways linking the four distinct states of the active site and the associated substrate reactions. (b) Surface dynamics of conversion of *n*-butane to maleic anhydride on one four-fold cluster of active sites on $(VO)_2P_2O_7$.

(i.e. a reduction in yield of at least 30–70 fold) but drops only by a factor of ~ 2–3 over the V_2O_5 and $CoMoO_4$ catalysts. However, it is important to note that while at longer *n*-butane contact times even nitrous oxide is capable of supporting *n*-butane oxidation over vanadyl pyrophosphate, (e.g. at 450°C and ~ 3.5 s contact time, the *n*-butane conversion was ~ 18%) the selectivity to maleic anhydride is much lower (~ 30%). This is consistent with our postulate that the active site can be ultimately transformed from state S_2 to state S_3 by activated diffusion of the adsorbed oxygen atoms.

We considered several alternate explanations of our results but found them to be unsatisfactory. For example, we found no decomposition of nitrous oxide to nitrogen and dioxygen over any of the three catalysts that we tested, thus the difference in *n*-butane conversion could not have its origins in the difference in reactivity of the nitrous oxide itself. We also found that the vanadyl pyrophosphate catalyst was not greatly altered, when it was placed in an atmosphere containing nitrous oxide instead of oxygen since its selectivity to maleic anhydride was essentially the same before and after the experiment and the XRD-pattern of the V–P–O catalyst at the end of this series of experiments showed that it was essentially pure phase $(VO)_2P_2O_7$.

5. Conclusions

We compared the efficacy of molecular oxygen and nitrous oxide, N_2O, as oxidants for the oxidation of *n*-butane over $(VO)_2P_2O_7$, 50% V_2O_5/SiO_2 and 10% $CoMoO_4/TiO_2$. The results reveal that both these gases readily, but not selectively, oxidize *n*-butane over V_2O_5 and $CoMoO_4$. In marked contrast, only molecular oxygen, effectively and with high selectivity, oxidizes *n*-butane to maleic anhydride over $(VO)_2P_2O_7$, while N_2O does not oxidize *n*-butane at all over this catalyst.

We interpret this result in terms of a new mechanism which we have formulated to model the dynamics of the highly selective conversion of *n*-butane to maleic anhydride on the surface of vanadyl pyrophosphate. According to this mechanism, each dimeric active site on the surface of the vanadyl pyrophosphate catalyst can assume four distinct states that differ from each other in the number and nature of the available oxygen. The active sites are isolated in clusters of four by the presence of excess phosphorus, present on the surface in the form of pyrophosphate groups that serve as diffusion barriers to prevent excess oxygen from reaching the reactive surface bound intermediates. The initial step of *n*-butane activation involves a "pseudo-ozonide" structure formed from a vanadyl group and a dioxygen molecule chemisorbed on an adjacent vanadium atom. This unusual species is responsible for the initial activation of the *n*-butane, which occurs when the chemisorbed dioxygen abstracts an H-atom from the alkane and the adjacent metal-oxo group reacts with the incipient alkyl radical to form an alkoxy group. Subsequent transformations of the surface bound intermediates involve the participation of dioxygen adsorbed on adjacent sites. Dioxygen is thus an obligatory oxidant in this very selective reaction.

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