MILD OXIDATION OF *n*-BUTENES OVER MIXED TIN—VANADIUM OXIDES

By

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The oxidation of *n*-butenes in the gaseous phase over mixed oxide catalysts V_2O_5—SnO_2 has been investigated in a pulse reactor at 523—673 K. The main products of the reaction are acetaldehyde and acetic acid; methyl ethyl ketone, butyraldehyde and other compounds are formed in smaller quantities. Maximum selectivity is found in the oxidation of 1-butene over catalysts in the composition interval $3:1 \gtrsim V_2O_5:SnO_2 \gtrsim 2:1$ at 523—573 K. Above 620 K the selectivity is independent of the nature of the initial butene. This can be explained in that a gas mixture of thermodynamic equilibrium is undergoing conversion, because of the rapid isomerization of the double bond-containing compounds. Formation of the main products can be interpreted by a mechanism including adsorption of 1-butene on a surface Brönsted acid site, oxidation of butylcarbonium ion by lattice oxygen, and oxidative cracking of the same surface ion; in the case of 2-butene, oxidation occurs only after isomerization to 1-butene.

Introduction

Heterogeneous selective oxidation is a practicable possibility for the processing of the C_4 fraction formed as a by-product of cracking. *n*-Butenes can be converted into 1,3-butadiene over Bi_2O_3—MoO_3 or SnO_2—Sb_2O_4 catalysts [1,2], or they can be oxidized into maleic anhydride (MA) over V_2O_5—P_2O_5 [3]. Little attention has been paid to conversion into saturated carbonyl compounds, because of the low selectivity, though the results of POPOVA and MILMAN [4] demonstrated that methyl ethyl ketone is formed with high selectivity from *n*-butenes over copper oxide.

The oxidation of *n*-butenes into acetic acid has been investigated by BROCKHAUS [5] over various transition metal vanadates and it has been found that the selectivity for acetic acid was nearly 70 % in the temperature range 513—543 K. The only side-reactions observed were total oxidation and the formation of small amounts of maleic anhydride, which contrasts with the results of other authors [6—8] who have described the formation of numerous by-products.

The gas-phase oxidation of 1-butene over unsupported V_2O_5 has been investigated by HAUFFE and ABD EL-SALAAM [9], who found that the yields of the main products (acetic acid and maleic anhydride) are correlated to the extent of reduction of the catalyst; this depends on the reaction temperature. The steady-state composition of the catalyst at 623 K, which has the highest selectivity, is $V_2O_{4,8}$; the catalyst is a solid solution containing V^{5+} and V^{4+}.

Although V_2O_5-based mixed oxide catalysts promote the formation of maleic anhydride during the mild oxidation of n-butenes [10, 11], in the presence of certain additives saturated carbonyl compounds such as acetic acid, acetaldehyde, methyl ethyl ketone and possibly propionic acid can be formed. KANEKO et al. [12, 13] investigated the relationship between the structure and the activity of V—Sn—W oxide catalysts for butene oxidation, and found that the effective catalyst, which has 40—60% selectivity for acetic acid, contains V_2O_5 and V_4O_9 phases simultaneously, the optimum atomic ratio V^{5+}/V_{total} being 0.65. As concerns the mechanism of acetic acid formation, it has been proposed [14] that AcOH is mainly formed from acetaldehyde, which in turn is produced through the direct reaction of the active O species with the carbonium ion formed from the olefin on the acidic sites of the catalyst. The authors suggest that both isomerization and oxidation reactions take place on the same Brönsted acidic sites, which result from lattice defects of the catalyst. In connection with the acid-base properties of V_2O_5-based binary catalysts, mention must be made of the work of AI [15, 16], who studied the relation between the acidity of the catalyst and the selectivity for maleic anhydride; in the V_2O_5—SnO_2 system the highest acidity was measured for the catalyst with atomic ratio V:Sn = 1:1, which proved to be the most effective catalyst in the production of maleic anhydride.

The rates of oxidation of C_3H_6, C_2H_4, C_3H_8 and CO have been investigated by ONO et al. [17] over V—Sn oxides of various compositions. The catalytic activity exhibits two maxima at very different compositions, and it has been proposed that different oxygen species are responsible for the oxidation. For the catalyst with atomic ratio V/Sn = 2/1 an amorphous material has been found from which lattice oxygen is easily released. The activity maximum for the oxide with V/Sn = 1/8 is associated with the presence of V^{4+} ions dissolved in SnO_2. The presence of V^{4+} ions appears to faciliate the formation of adsorbed oxygen species, which play a significant role in the oxidation reaction.

Although the basic features of the mild oxidation of olefins over V_2O_5—SnO_2 have been clarified in previous work, the overall picture is still somewhat inconsistent and incomplete. The present paper, connected with studies on mild oxidation over SnO_2-based mixed oxide catalysts [18 19], deals with the oxidation of n-butenes over SnO_2—V_2O_5. We set out to establish catalyst compositions suitable for the production of saturated carbonyl compounds, and the optimum reaction conditions.

Experimental

The oxidation of n-butenes over pure V_2O_5, pure SnO_2, and their mixtures in various ratios, was investigated in a pulse reactor, while isomerization was studied in a recirculatory flow reactor. V_2O_5 was prepared from ammonium metavanadate by calcination at 623 K. For the preparation of SnO_2, metallic tin was dissolved in conc. HCl. Tin (IV) hydroxide was precipitated with NH_4OH, then washed and dried. The binary oxides were prepared by mixing the respective components in the correct proportions, followed by calcination at 873 K for 6 hours.

The thermal behaviour of the catalysts was investigated by derivatography (Q Derivatograph, MOM) and X-ray diffraction (DRON—3, USSR).

The microcatalytic reactor was made of stainless steel in a heated aluminium block

situated in a CHROM—4 gc unit. The reactor contained 0.5 g catalyst. The conditions selected (if not stated otherwise) were: pulse volume: 3 cm^3; composition: $C_4H_8:O_2:N_2 = 1:3:11.2$; flow rate of N_2 carrier gas: 0.4 cm^{3}s^{-1}; and pressure: 10^5 Pa.

For gc analysis, a 2.5 m column was used containing Carbowax 20M and phosphoric acid as stationary phase on Chromosorb W.

n-Butene isomerization measurements were carried out in a recirculatory flow reactor 243 cm^3 in volume. Product compositions were determined by gc analysis on samples withdrawn through a 0.5 cm^3 sampling valve at regular intervals. For separation of the components, a 2.5 m column containing dinonyl phthalate on Chromosorb W was used.

Results

Thermal analysis of the catalysts

Figure 1 depicts DTA curves of the pure and mixed oxides. The DTA curve of pure V_2O_5 displays three endotherms. The first, at 203 K, is a result of the loss of adsorbed and structural water; this peak is observed only in the case of samples 2 and 3 indicating the absence of water from catalysts with higher tin contents. The peak at 963 K corresponds to the melting of V_2O_5. In the case of samples 3, 4, and 5 there are endothermic and exothermic peaks above the melting point of V_2O_5. Since no loss of weight was found in this range, these peaks relate to the formation of a new compound, probably tin vanadate.

The formation of a new compound (and possibly a new phase) is proved by X-ray diffraction measurements. New peaks can be found in the X-ray diffraction patterns of the catalysts calcined at various temperatures, but new compound formation is inextensive, for the original peaks of V_2O_5 and SnO_2 remain dominant. Calcination above 973 K does not cause any further change in the structure of the catalyst.

Fig. 1. DTA curves for catalysts of different compositions (heating rate 10 K/min)
Compositions: 1. V_2O_5;
2. $V_2O_5:SnO_2 = 3:1$;
3. $V_2O_5:SnO_2 = 2:1$;
4. $V_2O_5:SnO_2 = 1:1$;
5. $V_2O_5:SnO_2 = 1:2$;
6. $V_2O_5:SnO_2 = 1:3$; 7. SnO_2

Oxidation of n-butenes

In the oxidation of *n*-butenes in a pulse reactor, the applied catalysts were characterized by the conversion (x) (the ratio of the oxidized and initial amounts of butene) and by the selectivity (y) (the ratio of the amount of a given product to the amount of butene oxidized). Average conversion and selectivity values for different catalysts and reaction conditions were calculated by using data obtained from the 4th—5th pulse on, which practically correspond to a stationary state.
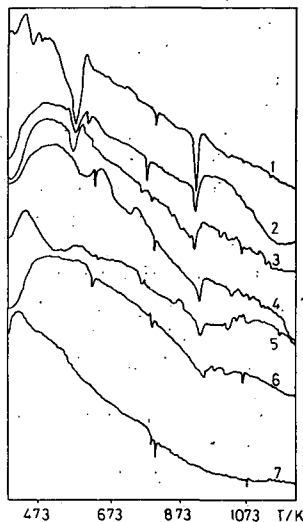
Properties of the catalysts as a function of composition

Since the properties of the mixed oxide catalysts used in the mild oxidation reactions are not the additive resultants of the properties of the pure components, we investigated how the properties change as a function of composition.

For the oxidation of both *n*-butenes, the conversion depends only slightly on the composition of the catalyst; maximum conversion is attained at a tin content of 75—30%.

During the oxidation, acetaldehyde and acetic acid are obtained as main products. Methyl ethyl ketone, butyraldehyde, propionaldehyde, propionic acid, crotonaldehyde, acrolein and some other products are also formed in small quantities.

The selectivity for acetaldehyde (one of the main products) formation as a function of the catalyst composition is shown at three different reaction temperatures in Fig. 2. Over the catalyst with $V_2O_5:SnO_2 = 3:1$, this selectivity is higher than 50%, but in the range $1:1 \gtrsim V_2O_5:SnO_2 \gtrsim 1:2$ and over pure SnO_2 an insignificant amount of acetaldehyde is found.

The selectivity for acetic acid (the other main product) can be seen in Fig. 3. Over pure SnO_2, acetic acid is not formed, and its quantity does not attain 1% in the catalyst composition range $1:1 \gtrsim V_2O_5:SnO_2 \gtrsim 1:2$. However, the selectivity reaches 30—35% at ratios $4:1 \gtrsim V_2O_5:SnO_2 \gtrsim 2:1$. During the oxidation, butyraldehyde is produced in relatively large amount. The appearance of this C_4 saturated aldehyde deserves particular attention, as its formation in this reaction has never been described before. Its selectivity as a function of composition is shown in Fig. 4. The course of the curve is similar to the previous ones, with the difference that butyraldehyde is formed in appreciable amount over pure SnO_2. The quantity of methyl ethyl ketone as a function of catalyst composition can be seen in Fig. 5. This is the second C_4 satura-

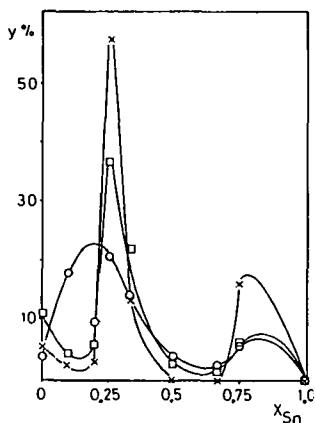*Fig. 2.* Selectivity for acetaldehyde as a function of catalyst composition in the oxidation of 1-butene $T_{reaction} = x$: 523 K; □: 598 K; ○: 673 K
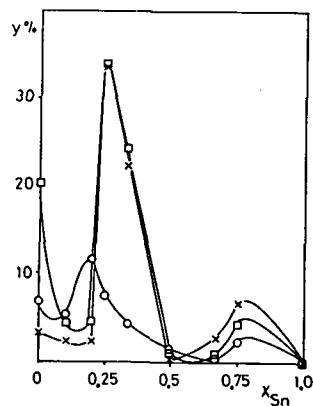

Fig. 3. Selectivity for acetic acid as a function of catalyst composition in the oxidation of 1-butene. ($T_{reaction}$ are the same as in Fig. 2)

ted carbonyl compound formed in large amount. The formation of butyraldehyde and methyl ethyl ketone can be explained by the participation of Brönsted-type acidic surface sites, in a carbonium ion mechanism [20].
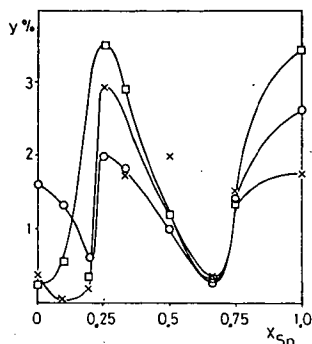

Fig. 4. Selectivity for butyraldehyde as a function of catalyst composition in the oxidation of 1-butene ($T_{reaction}$ are the same as in Fig.2)
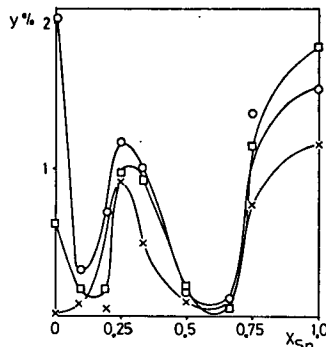
Fig. 5. Selectivity for methyl ethyl ketone as a function of catalyst composition in the oxidation of 1-butene ($T_{reaction}$ are the same as in Fig. 2)

Conversion and selectivity as functions of reaction temperature

At all reaction temperatures, the conversions in the oxidation of 1-butene over pure V_2O_5 and SnO_2 are much higher than the conversions of 2-butene, but the products are obtained in small amounts. Maximum selectivity in the oxidation of 1-butene has been found over the mixed oxide $V_2O_5:SnO_2 = 3:1$. In Fig. 7, the conversions and the selectivities for the main products (acetic acid and acetaldehyde) are shown as functions of the reaction temperature. At low temperatures the conversion increases sharply, attains a maximum at 623 K, and then decreases. In the range 523—573 K, the quantities of acetaldehyde and acetic acid are each about 50%. The selectivities for these products decrease as the reaction temperature increases, and total oxidation resulting in CO_2 becomes dominant.

The difference between the oxidation of 1- and 2-butenes is illustrated in Figs. 6, 8. The conversion over the mixed oxide $V_2O_5:SnO_2 = 1:1$ is shown as a function of temperature in Fig. 6. At low temperatures (below 623 K), 2-butene is oxidized less extensively than 1-butene, which undergoes 31—38% conversion in the temperature interval considered. The conversion of 2-butene depends strongly on the reaction temperature; at 523 K it is 18%, whereas at 673 K it is over 70%.
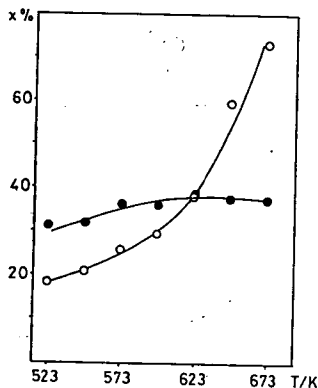

Fig. 6. Temperature-dependence of conversion in oxidation of 1-butene (●) and 2-butene (○) over $V_2O_5:SnO_2 = 1:1$

A comparison of the selectivities in the reactions of the two *n*-butenes revealed a great difference at low temperature (Fig. 8), but above 623 K the products and their selectivities are practically the same, independently of the initial compound. Below 623 K, the oxidation of 1-butene is more selective, with 2-butene the selctivity for each product being less than 20%.
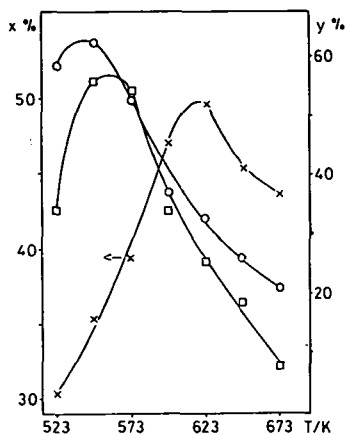
Fig. 7. Temperature-dependence of 1-butene oxidation over $V_2O_5:SnO_2 = 3:1$ (x: conversion, ○ selectivity for acetaldehyde, □: selectivity for acetic acid)
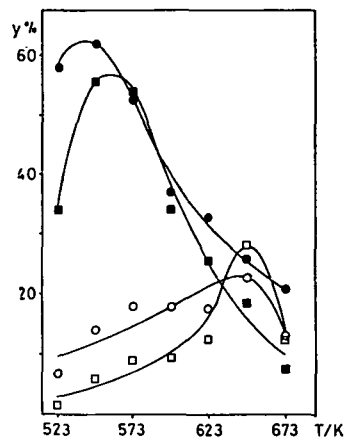
Fig. 8. Temperature-dependence of selectivity for acetaldehyde (○ ●) and acetic acid (□ ▨) in the oxidation of 1-butene (● ▨) and 2-butene (○ □) over $V_2O_5:SnO_2 = 3:1$

Isomerization of n-butenes

The identical selectivities point to the rapid occurrence of isomerization of the *n*-butenes, especially above 623 K. Accordingly, the isomerization of 1- and 2-butenes was studied over $V_2O_5:SnO_2 = 3:1$ at 473 K and 523 K in a recirculatory flow reactor, in the absence of dioxygen. The results are to be seen in Figs. 9—10. For both
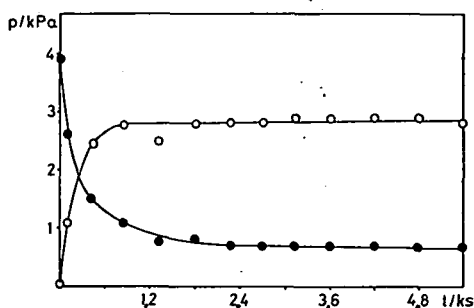
Fig. 9. Double bond isomerization of 1-butene over $V_2O_5:SnO_2 = 3:1$ at 523K; $p^0_{1-butene} = 4$ kPa; ● : 1-butene; ○ : 2-butene
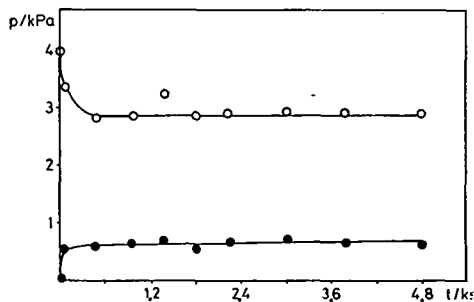
Fig. 10. Double bond isomerization of 2-butene over $V_2O_5:SnO_2 = 3:1$ at 523 K; $p^0_{2-butene} = 4$ kPa; ● : 1-butene; ○ : 2-butene

starting substances the reactants reach thermodynamic equilibrium in less than 10 minutes. At higher temperatures (above 623 K), the rate of isomerization is probably larger than the rate of oxidation, so that a reaction mixture in thermodynamic equilibrium (ca. 25% 1-butene and 75% 2-butene) is involved in the oxidation. The isomerization was investigated above 523 K too, but the results were difficult to interpret, as the catalyst was reduced by the olefins.

Discussion

The pulse reactor measurements show that 1-butene can be converted into acetaldehyde and acetic acid with high selectivity over the mixed oxide V_2O_5:$SnO_2 = 3:1$ in the temperature range 523—573 K. Comparison of the oxidations of the two *n*-butenes demonstrates that both the conversion and the selectivity for useful products are lower in the oxidation of 2-butene at low temperature than in that of 1-butene. However, above 623 K the selectivities yielded by the two *n*-butenes are practically the same. This can be explained in that the rate of double bond isomerization is much larger than the rate of oxidation at higher temperature, so that the oxidation involves a reaction mixture of *n*-butenes in thermodynamic equilibrium. Below 623 K (when the rate of isomerization is commensurable with or less than the rate of oxidation), 1- and 2-butenes behave differently. Under these circumstances the oxidation of 1-butene is more rapid and the selectivity is much higher too. It must be assumed that the two components are adsorbed in different ways and that two different species are formed on the catalyst surface, these species yielding products characteristic of the initial reagents. The formation of acetaldehyde and acetic acid from 2-butene can be explained by associative adsorption with cracking of the double bond [21]:

$$CH_3-CH=CH-CH_3 \text{ (gas)} \longrightarrow CH_3-\overset{\displaystyle +}{CH}-\underset{\displaystyle |}{CH}-CH_3$$
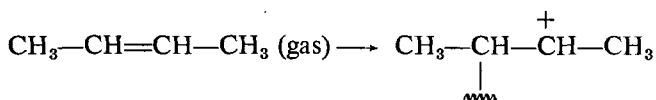
Interaction of the surface species and an O^{2-} ion gives

$$CH_3-CH-\overset{\displaystyle O^-}{\underset{\displaystyle |}{CH}}-CH_3$$
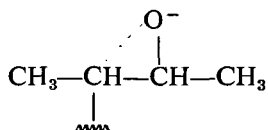
Further oxidation of this surface ion leads to acetaldehyde and acetic acid. However, our measurements indicate that oxidation of 1-butene into acetaldehyde or acetic acid cannot be explained either by associative adsorption or by π-type adsorption; in this latter case allyl-type unsaturated products such as 1,3-butadiene are formed. Associative adsorption resulting in cracking of the double bond would give propionaldehyde and propionic acid in the oxidation of 1-butene, but we found only small amounts of these products. Since the oxidation of 1-butene is more rapid than that of 2-butene, 2-butene formed by double bond isomerization is inconceivable as a transition product. The formation of acetic acid in the oxidation of 1-butene over transition metal oxides has been explained by two types of mechanism. KANEKO et al. [14] found that oxidation takes place over acidic sites resulting from lattice defects on the cata-

lyst surface. YAMASHITA et al. [22], however, concluded that hydration and oxidation steps play a significant role in this reaction and *sec*-butanol, methyl ethyl ketone and diacetyl were proposed as transition products. Both mechanisms assume the same transition products in the reaction of 1-butene and 2-butene, and similar rates of oxidation too.

In our opinion, both the formation of C_2 and C_4 carbonyl compounds in the oxidation of 1-butene can be described by a carbonium ion mechanism, the first step of which is the adsorption of the olefin on a surface site containing an —OH group. This reaction therefore takes place over a catalyst containing Brönsted acid sites capable of further oxidizing the surface carbonium ion. V—Sn mixed oxide catalysts contain Brönsted acid sites. Ai [16] reported that the acidity depends considerably on the composition. Maximum acidity was found for the mixed oxide containing 50% vanadium, and this catalyst seemed to be the most active in the oxidation of 2-butene into maleic anhydride. However, in accordance with our results, this mixed oxide did not prove to be selective in the oxidation of 1-butene. As concerns the relation between the identification of the oxidation centres, the structure of the catalyst, and the properties displayed in mild oxidation reactions, it can be stated that the selectivities given by the pure oxides are much lower than those with certain mixed catalysts. The derivatographic and X-ray diffraction results revealed that a new compound, tin vanadate, is formed only above the temperature of calcination of the catalyst. Hence neither the pure oxides nor the new phase is responsible for the selectivity. On the other hand, it can be assumed that the presence of the phase V_6O_{13} mentioned by ANDERSSON [23] results in the sele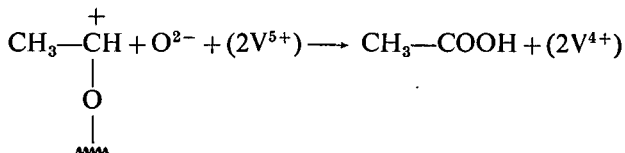ctivity. The role of SnO_2 is to weaken the surface V=O bonds, thereby mobilizing the lattice oxygens and promoting the incorporation of oxygen into the products.

Thus, the oxidation of 1-butene over V_2O_5—SnO_2 can be explained by the following mechanism. The first step is the adsorption of 1-butene on a surface acidic site:

$$CH_2=CH-CH_2-CH_3 \ + \quad \overset{\overset{H}{|}}{\underset{\underset{\text{ww}}{|}}{O}} \quad \overset{\nearrow}{\searrow} \quad \begin{array}{l} \overset{+}{CH_2}-CH_2-CH_2-CH_3 \quad (I) \\ \quad\quad \underset{\underset{\text{ww}}{|}}{O} \\[4pt] \overset{+}{CH_3}-CH-CH_2-CH_3 \quad (II) \\ \quad\quad \underset{\underset{\text{ww}}{|}}{O} \end{array}$$

During the chemisorption, two kinds of carbonium ion can be formed on the surface; these are attached *via* the oxygen of the —OH group. Reaction between *via* 1-butyl-carbonium ion (I) (the formation of which is much less probable than that of the 2-butylcarbonium ion (II)) and O^{2-} of the lattice results in butyraldehyde:

$$I + O^{2-} + (2V^{5+}) \longrightarrow CH_3-CH_2-CH_2-CHO + H + (2V^{4+})$$

lattice oxygen　　　　　　　　butyraldehyde　　　　　　　　　$\underset{\underset{\text{ww}}{|}}{O}$

In the similar reaction of the 2-butylcarbonium ion, methyl ethyl ketone is formed:

$$II + O^{2-} + (2V^{5+}) \longrightarrow \underset{\text{methyl ethyl ketone}}{CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - CH_3} + \underset{\overset{|}{O}}{H} + (2V^{4+})$$
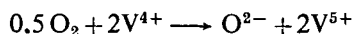
However, oxidative cracking is more probable in the reaction of the 2-butylcarbonium ion, with the formation of ethyloxonium ions:

$$II + 2O^- + (2V^{5+}) \longrightarrow \underset{\overset{|}{O}}{CH_3 - \overset{+}{C}H} + \underset{\overset{|}{O}}{\overset{+}{C}H - CH_3} + \underset{\overset{|}{O}}{H} + (2V^{4+})$$

Desorption of the ethyloxonium ion results in the formation of acetaldehyde, and further oxidation leads to acetic acid:

$$\underset{\overset{|}{O}}{CH_3 - \overset{+}{C}H} + O^{2-} + (2V^{5+}) \longrightarrow CH_3 - COOH + (2V^{4+})$$

Gaseous dioxygen plays an important role in reoxidation of the catalyst:

$$0.5 O_2 + 2V^{4+} \longrightarrow O^{2-} + 2V^{5+}$$

Adsorbed oxygen enters the lattice in this way and subsequently participates in the reaction as lattice oxygen.

Selective product formation in the reaction of 2-butene is due to double bond isomerization; 2-butene is first converted into 1-butene, which yields acetaldehyde and acetic acid *via* the mechanism desribed above. Saturated C_2 and C_4 carbonyl compounds can be formed only in the oxidation of 1-butene.

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ЧАСТОЧНОЕ ОКИСЛЕНИЕ Н-БУТЕНОВ НАД СМЕШАННЫМИ ОЛОВО-ВАНИДИЕВЫМИ ОКСИДАМИ

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Изучено окисление н-бутенов в газовой фазе над смешанными оксидными катализаторами V_2O_5—SnO_2 в импульсном реакторе при температурах 523—673 К. Основными продуктами являются ацетальдегид, уксусная кислота, метилэтилкетон, бутиральдегид, а другие продукты образуются в меньших количествах. Наибольшая селективность в окислении 1-бутена найдена над катализаторами с сотавом $3:1 \geqq V_2O_5:SnO_2 \geqq 2:1$ в интервале температур 523—573 К. Выше температуры 620 К селективность реакции не зависит от строения исходного бутена.