

Investigations of Catalytically Active Surface Compounds

XVII. Influence of Size and Structure of Vanadium Oxide Clusters on Selectivity in the Oxidation of *n*-Butene

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n-Butene oxidation on vanadium oxide monolayer catalysts (supported on Aerosil-200) was investigated in the temperature range from 633 to 693 K using two types of active vanadium oxide components differing with respect to the size of the clusters and the coordination of the vanadium ions. Coordination is characterized by uv-vis spectroscopy. The degree of reduction of vanadium in a state close to reaction conditions was determined by titration of suitably pretreated samples. In the conversion range between 7 and 95%, selectivities for butadiene, furan, maleic anhydride, acetaldehyde, CO, and CO₂ were determined, initial selectivities S^0 being estimated by extrapolation to zero conversion. A formal reaction scheme including direct formation of products without desorption and readsorption of preceding intermediates is proposed. From comparison of the values of S^0 and κ (ratio of rate constants for formation and consumption of primary products) characteristic features of the different catalytic behavior of the two active surface phases have been derived. Selectivity is mainly influenced by the amount and the nature of oxygen available in the cluster, by the bond strength of oxygen in the cluster unit, and by the probability of formation of radical oxygen species. © 1985 Academic Press, Inc.

INTRODUCTION

Results of the investigation of the selective oxidation of *n*-butene using oxides of the transition metals as massive or highly concentrated supported catalysts have been described in various papers (1-8). In many of these cases vanadium oxide, sometimes combined with further oxides, was chosen as the catalytically active component. Characterization of surface phases of vanadium oxide layered on Aerosil in a high dilution (containing approx. 1 wt% of V) revealed that, depending on the density and the topology of the silanol groups of the support, in extreme cases two types of vanadium oxide clusters differing in size and coordination of the vanadium are formed on the surface of the support (9).

Previous studies of the oxidation of ethanol and *n*-butene have shown that these vanadium oxide surface clusters differ consid-

erably in their catalytic properties. Thus activity may vary by a factor of 20. Likewise significant differences are observed in the distribution of products formed by the reaction (10). The aim of the present paper is to present results of a more detailed investigation and to give a description of the influence of size and structure of vanadium oxide clusters on selectivities to various products of the reaction. Due to the formation of a broad range of compounds with different degrees of oxidative transformation, the oxidation of *n*-butene recommends itself as a test reaction.

EXPERIMENTAL

The catalysts used throughout the investigation were vanadium oxide supported on Aerosil and were of the monolayer type. Their preparation has been described elsewhere (9, 11). The concentration of the silanol groups on the Aerosil surface, which

controls the formation of the vanadium oxide surface phase, was fixed by appropriate choice of the temperature of pretreatment of the Aerosil. The values obtained were (12): 0.75 mmol/g for 520 K and 0.25 mmol/g for 1070 K. Four catalysts were examined. Apart from the standard contents of 0.8 wt% of vanadium, both types of clusters (or surface phases) are represented additionally by a sample containing a higher amount of the active component (Table 1).

Spectroscopic characterization was based upon uv-vis reflectance spectra using a Beckman DK-2A spectrophotometer with a reflectance attachment. Reference substances were either pure Aerosil-200 or a catalyst sample annealed previously at 920 K.

To determine the degree of reduction of vanadium layered on Aerosil original catalyst samples (0.5 g) were heated to 473 K in a glass tube in a mixed stream of oxygen, argon, and *n*-butene (flow rate 14 liters/h), held at 473 K for 60 min and subsequently heated to 623 K during 30 min. The composition of the gas could be varied from 7 to 80 vol% oxygen at a constant concentration of 1 vol% *n*-butene. The glass tube was supplied with a device permitting the transfer of the sample after thermal treatment within one second into a vessel cooled by liquid nitrogen and held under a flow of pure argon. After room temperature was reached vanadium oxide was dissolved in diluted H₂SO₄ under inert atmosphere and titrated with 0.05 N KMnO₄ solution.

The reactor used for the investigations was of the open CSTR type with internal gas circulation (13). The reaction temperature was varied between 633 and 693 K. A premixed gas containing 1.5 vol% of *n*-butene (butene-1: 91.5%, *trans*-butene-2: 2.2%, and *cis*-butene-2: 6.3%) in air was used. Changes of conversion from 7 to 95% were achieved by variation of the mean residence time, i.e., by variation of the flow rate of the gas mixture. Mathematical treatment of experimental values (conversion and selectivity) to calculate S^0 and κ (Table 2) was based on a computing technique. An unweighted least-squares procedure was used to estimate numeric parameters. A regularized Gauss-Newton method suggested by Marquard (30) was applied as a minimization strategy.

RESULTS

Spectroscopic Measurements

Charge-transfer (CT) spectra of V⁵⁺ ions (d^0) in the uv-vis region were recorded to characterize the structure of the active component in the catalyst samples. The value of the electron-charge-transfer energy, which is related to the maximum of absorption (minimum of reflectance), is strongly influenced by the number of ligands in the environment of the central ion and gives information on the coordination of the vanadium in the clusters (14).

Using Aerosil-200 as a reference substance, uv-vis spectra (Figs. 1a and b) were

TABLE 1
Catalyst Characteristics

Catalyst	Contents of active component (wt% V)	Annealing temp. of Aerosil-200 (K)	Vanadium cluster size	Surface phase of vanadium oxide
Ae(1070)V 0.8	0.80	1070	V ₁₀	Octahedral δ'
Ae(1070)V 2.0	1.97	1070	V ₁₀	Octahedral δ'
Ae(520)V 0.8	0.80	520	V ₃	Tetrahedral δ'
Ae(520)V 1.4	1.42	520	V ₃	Tetrahedral δ'

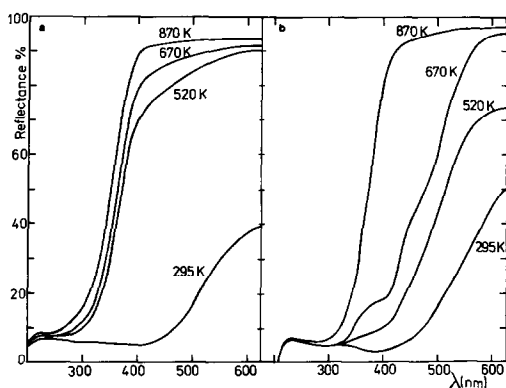


FIG. 1. The uv-vis reflectance spectra of samples Ae(520)V 0.8 (a) and Ae(1070)V 0.8 (b) in the original state after preparation (295 K) and after thermal treatment in air at 520, 670, and 870 K, the pure Aerosil preannealed at 950 K being used as a white reference substance.

observed to be similar to those obtained earlier (9) for highly diluted vanadium oxide. In the original state after preparation, with water still adsorbed, Ae(1070)V 0.8 and Ae(520)V 0.8¹ show spectra analogous to crystalline V₂O₅ (9). This means that V⁵⁺ ions possess octahedral coordination, due either to a complete saturation of the coordination sphere by constitutional O²⁻ ions (Ae(1070)V 0.8) or to the presence of H₂O ligands (Ae(520)V 0.8). On raising the temperature (to 520 K) in a dry stream of air, adsorbed water is removed: catalyst Ae(1070)V 0.8 (Fig. 1b) still shows the minimum of reflectance at 400 nm, related to the unchanged octahedral decavanadate-like coordination for V⁵⁺, whereas the removal of water shifts the absorption edge of the Ae(520)V 0.8 catalyst (Fig. 1a) toward wavelengths lower than 350 nm, which characterize tetrahedrally coordinated V⁵⁺ (9).

The distinction between the two types becomes even clearer with the so-called difference spectra. These are obtained if a highly annealed sample (920 K) of the cata-

¹ Notations have the following meaning: Ae = Aerosil, (1070) = annealing temperature in K, V = vanadium, 0.8 = weight percent of vanadium (as vanadia) supported on Aerosil (Table 1).

lyst under investigation is used as a reference substance instead of pure Aerosil-200. As is well known (9), at temperatures higher than 750 K a destruction of any microcrystallites of V₂O₅ on SiO₂ takes place giving rise to the formation of lower-coordinated, i.e., tetrahedral V⁵⁺ oxide units. If a sample with completely "tetrahedralized" vanadium oxide is introduced as a reference substance, exclusively deviations of a given sample from pure tetrahedral coordination are visible in the spectra (Figs. 2 and 3). Catalyst Ae(1070)V 0.8 (full lines) again shows clear octahedral behavior with a minimum of reflectance at 400 nm. The octahedral surface phase is destroyed at higher temperatures only (e.g., 770 K).

With catalyst Ae(520)V 0.8 (dotted lines), however, the minimum of reflectance at 400 nm characterizing octahedral coordination disappears already after calcination at 520 K; all the vanadium oxide then possesses tetrahedral coordination, even in the case

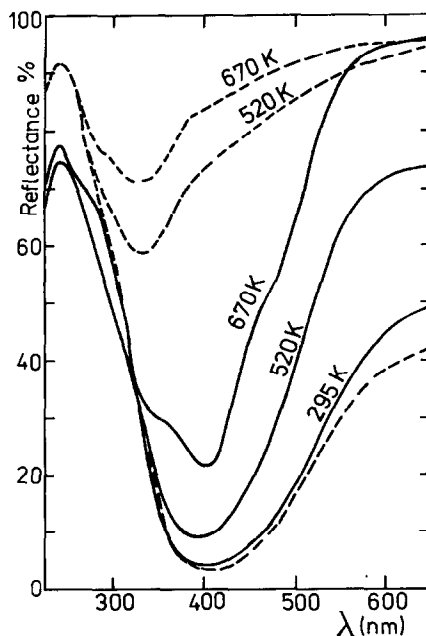


FIG. 2. The uv-vis reflectance difference spectra of samples Ae(520)V 0.8 (dotted line) and Ae(1070)V 0.8 (full line) at 295 K, and thermal treatment at 520 and 670 K, a sample of the same origin pretreated at 920 K being used as a reference substance.

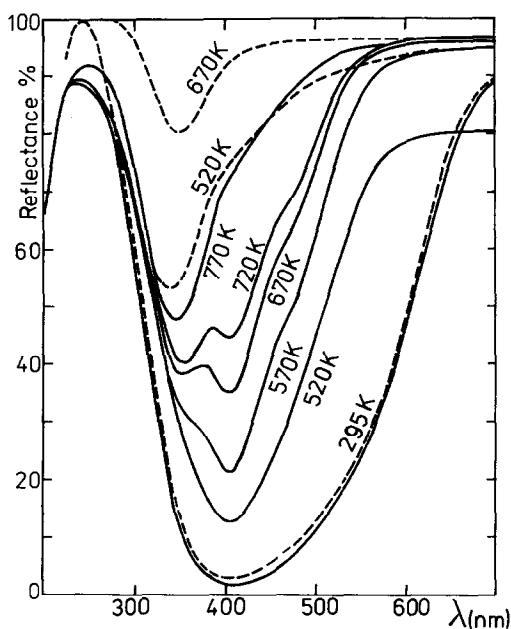


FIG. 3. The uv-vis reflectance difference spectra of samples Ae(520)V 1.42 (dotted line) and Ae(1070)V 2.0 (full line) at 295 K and thermal treatment at 520 and 670 K, a sample of the same origin pretreated at 920 K being used as a reference substance.

of higher V contents (1.42 wt%). The minimum in the region between 325 and 350 nm is due to a small portion of a highly aggregated nonoctahedral kind of vanadium oxide. This species is also detectable as a transient state during conversion of decavanadate-like V oxide into tetrahedrally coordinated vanadium oxide at high temperatures.

It is worth mentioning that the absence of octahedral coordination for catalysts supported on Aerosil pretreated at 520 K is limited to maximum amounts of vanadia not exceeding 1.42 wt% of vanadium.

The absence of any absorption above 550 nm in the case of unreacted catalysts demonstrates that V^{4+} is not present. In the spectra of catalysts recorded after reaction, however, strong absorption in the range between 550 and 1000 nm occurs, which is due to reduced vanadium ions (15).

As was derived from chemisorption data of *n*-butene (10) the number of octahedrally

coordinated vanadium ions contained in one cluster unit amounts to 10 or 11 (V_{10} -clusters, δ'' -phase), whereas clusters of the tetrahedrally coordinated surface phase comprise three vanadium ions only (V_3 -clusters, δ' -phase).

Catalytic Measurements

As with many gas phase oxidations, oxidation of *n*-butene produces a wide range of compounds (1-8). In the present case 12 compounds could be identified by gas chromatography. Seven were chosen to characterize the dependence of selectivity on the degree of conversion, viz. butadiene (BD), furan (F), acetaldehyde, acetic acid, maleic anhydride (MA), CO, and CO_2 . By extrapolating to zero conversion, values of initial selectivities (S^0) could be estimated. As their relative amounts were too low, other compounds identified among the products (acetone, acrolein, methyl ethyl ketone, crotonaldehyde, methacrolein) had to be excluded from the considerations which follow. The different catalytic behavior of

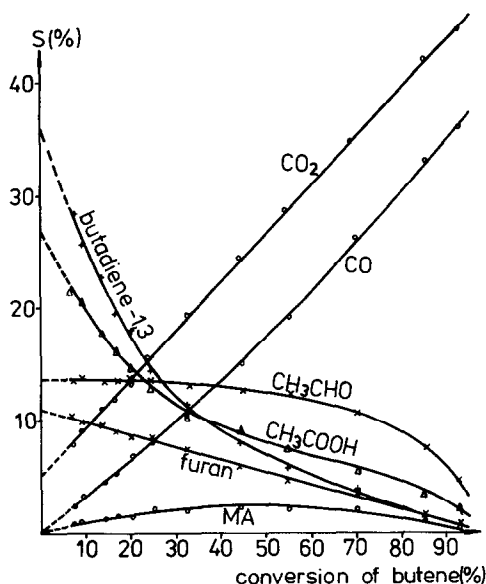


FIG. 4. Dependence of selectivities on the percentage degree of conversion, catalyst Ae(520)V 0.8, reaction temperature: 693 K.

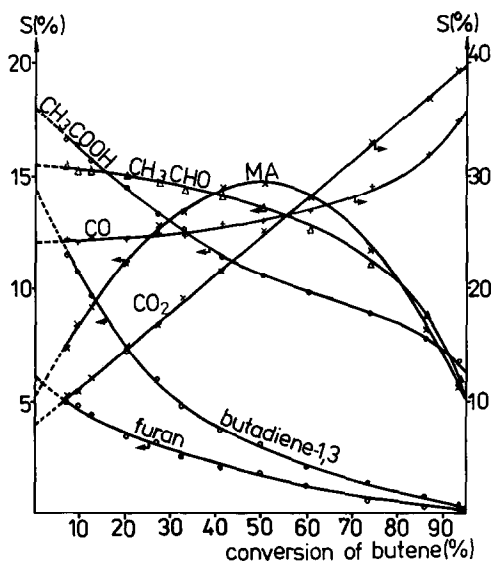


FIG. 5. Dependence of selectivities on the percentage degree of conversion, catalyst Ae(1070)V 0.8, reaction temperature: 693 K.

the two surface phases is mainly expressed by (Figs. 4 and 5):

—the differences of the initial selectivities for butadiene: 15% for δ'' in comparison with 35% for δ' ;

—the absence of CO and maleic anhydride in the initial period of the reaction in the case of δ' .

For both catalysts, butadiene, furan, and acetaldehyde are primary products, exposed to further reactions. The decreasing S-shaped selectivity curve of acetic acid points to the fact that its primary formation (accompanied by consumption) is supplemented by secondary formation as conversion is raised. CO₂ is a stable final product of the direct oxidation of *n*-butene. In addition, it occurs as a result of further oxidative degradation of intermediate compounds, as is shown by the continuously rising selectivity with increasing degree of conversion.

Maleic anhydride and CO are products of secondary oxidation. Additionally they are primary products for the δ'' -catalyst. CO and CO₂ are stable products, while maleic anhydride undergoes further oxidation as the reaction proceeds.

The influence of the reaction temperature on the initial selectivities is shown in Table 2. Butadiene and furan are practically not affected by the temperature rise. The in-

TABLE 2

Values of S^0 and κ for Catalysts Investigated

Catalyst	Reaction temp. (K)	S_{BD}^0	κ_{BD}	S_F^0	κ_F	$S_{CH_3CHO}^0$	κ_{CH_3CHO}	$S_{CH_3COOH}^0$	S_{CO}^0	S_{MA}^0	$S_{CO_2}^0$
Ae(1070)V 0.8 0.8 wt% V	633	15.2	25.9	6.10	41.0	22.5	0.66	21.0	21.6	1.0	6.4
	653	14.5	26.2	6.00	38.3	19.4	0.78	20.0	23.0	2.0	7.0
	673	15.4	24.0	6.22	39.2	17.2	0.80	18.9	23.1	3.5	7.2
Ae(1070)V 2.0 1.97 wt% V	693	14.6	26.0	6.16	41.1	15.5	0.85	18.3	24.0	5.1	7.8
	633	14.9	28.8	3.26	52.0	16.1	0.76	18.9	24.6	3.0	8.7
	653	15.6	29.6	3.39	53.4	15.6	1.03	17.5	25.9	4.5	9.4
Ae(520)V 0.8 0.8 wt% V	673	14.0	32.7	3.10	59.7	14.6	1.25	16.1	26.7	6.5	9.7
	693	14.7	32.7	3.11	63.3	13.1	1.72	16.2	28.2	8.1	10.0
	633	35.0	9.83	10.8	9.26	16.8	0.48	28.0	none	none	4.5
Ae(520)V 1.4 1.42 wt% V	653	35.8	9.80	11.9	8.40	15.0	0.46	28.3	none	none	4.7
	673	35.8	9.69	11.4	8.77	14.7	0.52	27.4	none	none	4.9
	693	36.2	9.89	11.1	9.01	13.5	0.66	27.0	none	none	5.0
693	21.0	11.9	12.3	12.6	13.8	0.91	13.7	25.1	1.5	8.0	

Note. Mean confidence interval of S^0 and κ_i values for a 99% level of significance $\approx \pm 4.5\%$.

crease of products of further oxidation (S_{MA}^0 , S_{CO}^0 , and $S_{CO_2}^0$) with rising temperature is evident, and proceeds at the expense of acetaldehyde and acetic acid. The positive influence of temperature exerted on maleic anhydride is illustrated additionally by the selectivity/conversion curves (Fig. 6): for Ae(1070)V 0.8 the maximum value for MA reaches 15% as temperature rises.

Selectivities are also influenced by the amount of vanadium oxide layered on the surface. Increase of the quantity of the active component exhibits the stronger effect within the δ' -phase. In some respects there is an approach to the δ'' -phase: thus S_{BD}^0 decreases, $S_{CO_2}^0$ is raised, and CO and maleic anhydride appear among primary products, but S_F^0 retains a value characteristic for the δ' -phase.

The early appearance of stable compounds, usually considered as products of consecutive oxidation, has been explained by a so-called "rake"-mechanism (16, 17). It is based on the assumption that a portion of the chemisorbed organic reactant is converted to products of deeper oxidative transformation following a *direct* path, i.e.,

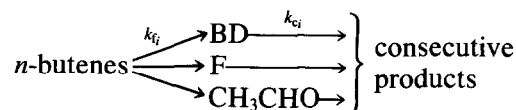
without desorption and readsorption of imaginable intermediates. These stable compounds then behave kinetically like primary products. The ratio κ_i of rate constants for their formation (k_{fi}) and consumption (k_{ci})

$$\kappa_i = \frac{k_{ci}}{k_{fi}} \quad (1)$$

can be calculated using the expression

$$\kappa_i = \frac{(S_i^0 - S_i)(100 - X)}{S_i \times S_i^0} \quad (2)$$

which is valid for a continuously stirred tank reactor (18). The values of selectivity (S_i) at a given percentage conversion of *n*-butene (X) for the three products butadiene, furan, and acetaldehyde formed by a direct path



are known from experiment (Figs. 4 and 5). The derivation of Eq. (2) presumes,

- that the order of reaction w.r.t. the organic reactant is unity;
- that the second reactant (O_2) is available in excess, guaranteeing that to a first approximation its concentration is constant during reaction;
- that any resistance terms in the kinetic equations for the steps of formation and consumption are identical.

The kind of dependence of the reaction rate on the stationary concentration of *n*-butene (13, 19) and the extremely small changes of gas phase partial pressure of oxygen as reaction proceeds indicate that the first two conditions are implemented. Identity of the type of the kinetic equation for two reaction steps succeeding one another has been assumed or even confirmed in similar cases (2, 20–22). The constancy observed for the values of κ_i over the whole range of conversion (Table 3) proves that at least to a good approximation the assump-

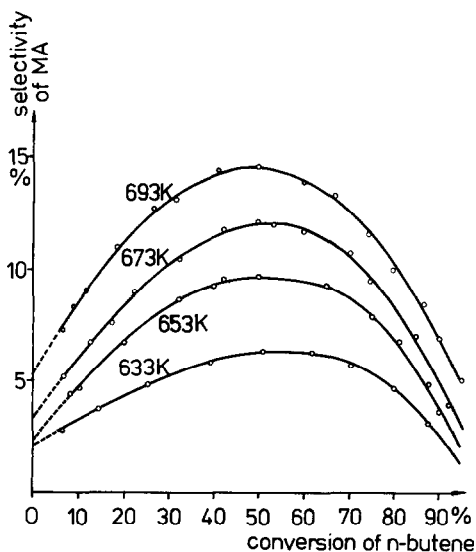


FIG. 6. Selectivity of maleic anhydride as a function of the percentage degree of conversion of butene and reaction temperature for catalyst Ae(1070)V 0.8.

TABLE 3
Influence of the Degree of Conversion on κ_i -Values Reaction Temperature: 693 K

Catalyst conversion (%)	Ae(1070)V 0.8			Conversion (%)	Ae(570)V 0.8		
	κ_{BD}	κ_F	κ_{CH_3CHO}		κ_{BD}	κ_F	κ_{CH_3CHO}
7.0	26.0	41.3	0.89	7.0	9.84	9.16	0.70
10.2	25.7	41.4	0.83	8.9	9.58	9.22	0.65
12.9	26.3	43.6	0.85	14.2	9.83	8.27	0.63
20.3	25.8	44.0	0.90	18.0	10.43	8.57	0.61
27.6	25.4	38.8	0.89	20.9	9.86	8.63	0.66
32.8	26.3	39.5	0.77	25.6	10.01	9.42	0.64
41.3	26.8	38.2	0.91	32.4	9.27	9.20	0.67
50.0	25.7	41.4	0.82	40.5	9.49	9.55	0.62
59.5	25.5	41.2	0.93	55.1	9.63	9.75	0.71
73.8	26.0	39.8	0.85	70.6	10.20	8.20	0.68
86.4	26.6	42.7	0.79	85.6	10.02	8.52	0.71
95.0	25.7	40.8	0.83	93.6	10.51	9.62	0.64
Average value:	26.0	41.1	0.85	Average value:	9.89	9.01	0.66

tion of identity is justified in the present case.

A further conclusion to be drawn from the fact that κ_i values do not depend on the degree of conversion is that all three compounds are formed *exclusively* by a direct path. Any amounts which might be produced during consecutive reactions lie within the boundaries of experimental accuracy.

The differences in catalytic behavior are more or less strongly reflected also by κ : the κ_i -values for V_3 clusters are distinctly lower than those for the V_{10} surface phase. The effect is strongest with furan, and κ_{CH_3CHO} shows small changes only. For V_3 clusters the relative stabilities of butadiene and furan under the conditions of reaction, as expressed by κ_i , become practically identical.

An increase of the *amount* of the active component causes an increase of κ_i . Thus the δ' surface phase slightly approaches the δ'' surface phase.

Changes of reaction temperature obviously do not provoke drastic shifts in the relations between the single steps of reaction. Deviations of κ_i values for samples

with 0.8 wt% of vanadium lie within the scattering range. The influence of reaction temperature becomes somewhat stronger if the amount of active component is increased (Ae(1070)V 2.0): κ_i -values then increase with rising temperature.

DISCUSSION

The mechanism of the reaction can be described by the scheme of Fig. 7. The dotted line indicates that this reaction path exists for the octahedral V_{10} clusters only.

The detection of primary products, the formation of which stoichiometrically demands more than one molecule of oxygen, is not an unusual observation in catalytic oxidations (1, 2, 3, 5, 23). Thus acetalde-

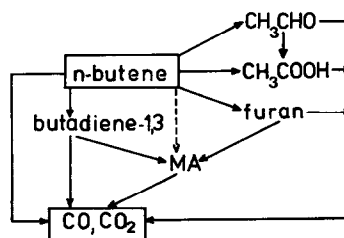


FIG. 7. Formal reaction scheme.

hyde, acetic acid, propionic acid, crotonaldehyde, methyl vinyl ketone (2) and maleic anhydride (3) have been found to be present already in the first stages of reaction. The appearance of furan among the primary products indicates that the direct path has general significance for selective oxidation and is not limited to total oxidation and oxidative degradation.

Secondary formation of furan via butadiene is not included in the scheme. In the present case it plays a negligible role, if any. Butadiene, a potential precursor of furan, is exposed to further oxidation and might be either totally oxidized or transformed to products of deeper oxidation, e.g., to maleic anhydride following a path proposed by Akimoto and Echigoya (24).

Comparison of the results for the two types of catalyst shows that with V_3 -clusters those primary products are favoured whose formation needs relatively small amounts of oxygen. This is expressed above all by the high values of S_{BD}^0 and S_F^0 accompanied by a sharp decrease of $S_{CO_2}^0$, S_{CO}^0 , and S_{MA}^0 (the latter two being zero). In the case of V_3 -clusters the succession of direct transformation of *n*-butene which can be understood in terms of the so-called methyl-allyl mechanism (1) is interrupted at the furan intermediate. Maleic anhydride, which is among primary products with the V_{10} -clusters, is not produced in the direct path on the V_3 -clusters. Oxidative splitting of butene, possibly started by an attack on the double bond, is stopped at the intermediate of acetic acid: further degradation producing CO_2 takes place to a small extent only, while that leading to CO is suppressed completely.

In the case of V_3 -clusters the probability of desorption of surface intermediates of minor oxidative transformation appears to be distinctly higher than that of their further oxidation. The main cause for this lies in the limited stock of constitutional oxygen in the smaller V_3 -clusters. Availability of oxygen is decreased additionally by its stronger bonding. As could be shown by preceding

studies of adsorption of oxygen on vanadium oxide catalysts, which have been previously reduced by hydrogen, the oxygen bond energies of V_3 -clusters lie 50 to 65 kJ/mol higher than those of V_{10} -clusters (25). The stronger bonding of oxygen in the V_3 -clusters is confirmed by differences in the reducibility of the two vanadium oxide surface phases under conditions close to catalytic reaction. In a gaseous atmosphere containing 1.5 vol% of *n*-butene in air, corresponding to an oxygen/butene ratio of nearly 13:1, a definitely lower degree of stationary reduction is reached in the case of V_3 -clusters, namely 10 to 15% in comparison to approximately 50% with V_{10} -clusters (Fig. 8).

The differences in the nature of the oxygen available in the clusters are reflected by the relation between selective and destructive oxidation as represented by the S^0 values. In the case of V_3 -clusters direct transformation of *n*-butene into the products of selective oxidation (butadiene, furan, and maleic anhydride) amounts to about 45%, a value which is definitely higher than the 22 to 25% characteristic for V_{10} -clusters. This difference confirms that the strong-bonded constitutional oxygen of the V_3 -clusters is more likely to favor selective oxidation than the oxygen of the V_{10} -clusters.

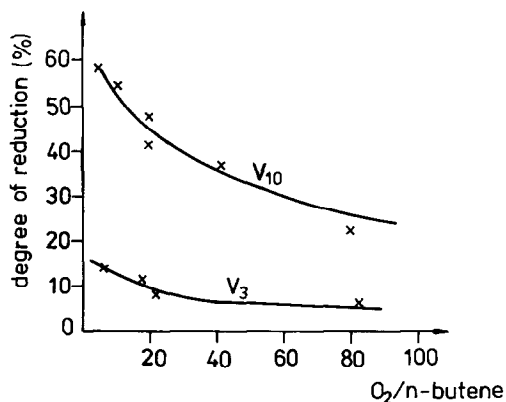


Fig. 8. Dependence of the percentage degree of reduction of vanadium (expressed as V^{IV}/V_{total}) on the composition of the adjacent gas phase, vanadium content of the sample 0.8 wt%, reduction period 1.5 h at 623 K.

With V_3 -clusters total oxidation is due above all to secondary reactions of intermediate products (butadiene, acetaldehyde, furan, acetic acid). For these clusters large amounts of adsorbed charged oxygen species are characteristic. As proved by ESR studies (26), under identical conditions (degree of reduction of the vanadium and partial pressure of oxygen in the ambient atmosphere); V_3 -clusters show a density of adsorbed O_2^- radicals which is many times higher than that detected on V_{10} -clusters. The formation of nondissociative oxygen species is confirmed by investigations of the adsorption of oxygen during the reoxidation of previously reduced vanadium oxide (27). The suggestion that tetrahedrally coordinated cations would be present in the centers at which adsorption of oxygen as O_2^- is favored has already been made in discussing results obtained with other metal oxides (28).

The high density of molecular oxygen species, which are known to favor destructive oxidation (29), can strongly influence the further oxidation of intermediate products following their readsorption at reoxidized clusters. Thus with V_3 -clusters the highly reactive butadiene (Table 4) and the furan are predominantly totally oxidized, whereas in the further oxidation of readsorbed intermediates on V_{10} -clusters with a lower density of O_2^- radicals the formation

of maleic anhydride is given a higher chance.

The changes in the values of selectivity for the δ' phase observed with the increase of the amount of active component are not caused by the presence of octahedrally coordinated vanadium oxide (Figs. 2 and 3). They may be related to the more dense coverage of the surface with vanadium oxide, thus reducing the distance between neighbouring V_3 -clusters or even giving rise to the appearance of tetrahedrally coordinated clusters of larger size (Fig. 3). The increased availability of oxygen results in an approach to a behaviour characteristic of the V_{10} -cluster catalysts: S_{BD}^0 decreases, and CO and maleic anhydride occur among the primary products. With the δ'' phase the higher density of V_{10} -clusters only slightly favors selective oxidation.

Partial oxidation with preservation of the number of C-atoms in the molecule is supported also by a temperature increase, as can be seen from MA-selectivity (Fig. 6). This can be understood by assuming that the incorporation of oxygen into the clusters (i.e., reoxidation of vanadium) is facilitated with rising temperature, thus driving back the influence of adsorbed (electrophilic) oxygen on the reaction. This explanation is confirmed by the results of the investigation of the kinetics of the reaction. Due to the high value of the energy of acti-

TABLE 4

Dimensionless Reactivity $k_{C_i}/k_{C_{n\text{-butene}}}$ for Butadiene, Furan, and Acetaldehyde Related to the Reactivity (Total Consumption) of *n*-Butene

Catalyst temperature	$\frac{k_{C_i}}{k_{C_{n\text{-butene}}}} = \frac{\kappa_i \times S_i^0}{100}$					
	Ae(1070)V 0.8			Ae(520)V 0.8		
	Butadiene	Furan	Acetaldehyde	Butadiene	Furan	Acetaldehyde
633 K	3.94	2.50	0.15	3.44	1.00	0.08
653 K	3.80	2.30	0.15	3.51	1.00	0.07
673 K	3.70	2.44	0.14	3.47	1.00	0.08
693 K	3.80	2.53	0.13	3.58	1.00	0.09

vation (131 kJ/mol) for the reoxidation of the vanadium in the V_{10} -clusters (19), which is the limiting step in the redox cycle, the resubstitution of constitutional oxygen in the clusters is markedly accelerated as temperature is raised. The advancement of selective oxidation, however, is confined to maleic anhydride; initial selectivities of butadiene and furan do not respond to the temperature increase.

The relationships experimentally observed and discussed above show that the nature of the clusters not only influences catalytic activity but *selectivity* as well. These relationships have turned out to be rather complex. The nature and the amount of the oxygen in the clusters and the different ways in which it interacts with the organic molecule are regarded as the essential means by which changes in the size and the structure of these clusters may affect the distribution of products formed in the reaction.

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