AN INVESTIGATION OF THE OXIDATIVE DEHYDROGENATION OF n-BUTENES OVER MIXED TIN-ANTIMONY OXIDES

By

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The oxidation of *n*-butenes in the gaseous phase over mixed oxide catalysts SnO_2—Sb_2O_4 was investigated in a pulse reactor and in a recirculatory flow reactor at 523—673 K. Over catalysts containing more than 50% tin, practically the total quantity of converted 1-butene was transformed into butadiene. The reaction of 2-butene depended to a considerable extent on the composition of the catalyst. The lowest conversion was found for the mixed oxide with Sn: Sb=1:1, but in the formation of butadiene this was the most selective catalyst. The selectivity decreased appreciably as the reaction temperature rose. From measurements in the recirculatory flow reactor, apparent rate constants and activation energies of reactions were determined; the latter values for 1-butene and 2-butene, were 105 and 70 kJ mol^{-1}, respectively. This difference was explained by the dissimilarity of the rate-determining steps in the two reactions. The oxidation of 2-butene precedes isomerization to 1-butene on surface acid sites, with subsequent conversion to butadiene on oxidation centres *via* a π-allyl surface intermediate.

Introduction

The modern techniques used for the production of butadiene are based on the dehydrogenation of C_4 hydrocarbons, the oxidative dehydrogenation of *n*-butenes assuming increasing importance. 1- and 2-butene originating from cracking and pyrolysis are available in large amounts, and can be converted into butadiene with high selectivity at low temperature (623—723 K) in a heterogeneous catalytic process.

Besides the well-known bismuth-molybdate [1, 2] and iron-antimonate [3], recently mixed tin-antimony [4, 5] oxide catalysts have been applied in oxidative dehydrogenation.

The oxidation of butenes to butadiene was investigated by SALA and TRIFIRO [4] over SnO_2—Sb_2O_4 catalyst; it was found that the selectivity increased from 40 to 93% as the Sb_2O_4 content in the SnO_2 increased, and maximum selectivity was observed at an antimony content of 5%. Not only the selectivity of oxidation, but also the rate of double-bond isomerization increased. It is interesting that the addition of steam inhibited the isomerization without affecting the oxidation.

The results of several authors [6, 7, 8] show that the rate of reaction over catalysts of different compositions depends on the partial pressures of both butene and dioxygen. The partial order for each reactant is about 0.5. SAZANOVA et al. [6] stated

5*

that the reaction can be described by a redox-type mechanism. TRIMM and GABBAY [7] preferred a Langmuir—Hinshelwood mechanism. TRIFIRO and PASQUON [8] considered that different types of kinetic equations fit the experimental data to a good approximation. MCATEER [5] presumed an adjacent Sb^{3+}—Sn^{4+} ion-pair as the active site in the oxidation of butene. These two ions have different electron densities, so they form a surface acid-base centre. The first step in the oxidation reaction takes place on a Sn^{4+} ion, with acidic character. A positively charged allyl ion is then formed, which attaches to the adjacent basic centre through a π- or σ-bond. Butadiene results from the π-allyl intermediate during a proton-abstraction step and the product can readily desorb from the highly basic centre. The allyl intermediate attached to the nucleophilic surface oxygen through a σ-bond yields products containing oxygen, such as methyl vinyl ketone. On the other hand, HERNIMAN et al. [9] assert that the acid-base character has no fundamental role in the catalytic properties of mixed tin-antimony oxides. They consider that the properties are much rather determined by the electrical behaviour of the surface. In the optimum catalyst surface there are antimony(III) ions and O^{2-} vacancies, which can be formed only as a result of calcination for several days above 1300 K.

Although the basic features of the oxidative dehydrogenation over SnO_2—Sb_2O_4 have been clarified previously, the overall picture is still somewhat inconsistent and incomplete. The present paper, connected with studies on the oxidation and ammoxidation of olefins over mixed tin-antimony oxide catalysts [10—12], therefore deals with the oxidative dehydrogenation of n-butenes. We set out to establish the optimum reaction conditions (such as the composition of the catalyst, the reaction temperature, and the composition of the feed) and to determine the kinetics of the reactions. A possible reaction mechanism is given for interpretation of the experimental data.

Experimental

The effects of SnO_2—Sb_2O_4 mixed oxides in the oxidation of butenes were investigated in a pulse reactor. Detailed kinetic studies were made in a recirculatory flow reactor.

The binary oxides were prepared by mixing the components SnO_2 and Sb_2O_4 in the desired proportions, followed by calcination at 873 K for six hours. To permit comparison with previous results, mixed oxides at some ratios were prepared by coprecipitation. A mixture of $SbCl_5$ and $SnCl_4$ in the required proportions was dropped into NH_4OH solution during stirring. The precipitate was filtered off, washed free of chloride and ammonia, dried and calcined as before. After calcination, catalysts were pressed into tablets by 10 MPa pressure, and the tablets were broken and sieved. The 0.1—0.3 mm fraction of the granules was applied in the catalytic investigations.

The thermal behaviour of the catalysts was investigated by derivatography (DERIVATOGRAPH-Q, MOM), and phase analysis was performed by X-ray diffraction (DRON-3, USSR). The surface areas of the catalysts were determined with the BET method *via* the dinitrogen adsorption isotherm at the temperature of liquid nitrogen.

The experimental equipment and procedures were described earlier [11, 12]. In each experiment 1 g of catalyst was used.

Analyses were carried out with a CHROM-4 and a CHROMATRON GCHF 18.3 gas-chromatograph; the column, 5 m long, was filled with dimethylsulpholane adsorbed to 30% on Chromosorb W (mesh 80—100). On this column, the reagents and products were separated in the sequence: 1-butene, *trans*-2-butene, *cis*-2-butene, butadiene.

Results

Characterization of SnO_2—Sb_2O_4 mixed oxide system

During investigations of the thermal behaviour of the catalysts by derivatography, it was found that the TG, DTG and DTA curves of the pure oxides display neither exotherms nor endotherms in the interval 298—1273 K; this is in accord with other results [13, 14]. During the investigation of catalysts with different compositions, there was no change either. This was confirmed by X-ray diffraction measurements, which showed no new phase or compound in the tin-antimony system. However, the possibility of the formation of a solid solution [4] or twin boundaries [15] in small quantity is not precluded. There is no difference between the properties of catalysts prepared by mixing or by coprecipitation.

The surface areas of the mixed oxides calcined at 873 K are shown in Table I, as a function of composition. The surface areas of samples with low tin content (0—50 atom%) are practically the same; they then increase up to 15 $m^2 g^{-1}$ as the tin content increases. However, this relatively small change cannot be responsible for change in the catalytic properties as a function of catalyst composition.

Table I
Surface areas of various mixed oxides

Sn:Sb	a $m^2 g^{-1}$
1:0	13.1
5:1	15.0
3:1	12.2
2:1	9.1
1:1	5.0
1:2	6.5
1:3	5.9
1:5	7.9
0:1	5.6

Investigation of oxidative dehydrogenation in a pulse reactor

In the oxidative dehydrogenation of *n*-butenes in a pulse reactor, the applied catalysts were characterized by the conversion (x) (the ratio of the reacted and initial amounts of butene) and by the selectivity (y) (the ratio of the amount of a given product to the amount of butene reacted). 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

The effect of the catalyst composition is demonstrated at 623 K and at 1.013 bar. The volume of the pulse was 3 cm^3. The volumetric composition of the gas feed was 7% C_4H_8, 18% O_2 and 75% N_2.

For the oxidation of 1-butene (Fig. 1), the conversion (apart from pure Sb_2O_4) increases almost linearly as the tin content increases. Maximum selectivity for butadiene, which is 90%, is attained at a tin content of 75—90%. The most important byproducts are 2-butene *(cis-trans)* and carbon oxides, which form during the total oxidation of 1-butene or butadiene. Under the same reaction conditions, the conversion and selectivity for 2-butene (Fig. 2) differ considerably from those for 1-butene. The conversion decreases up to a tin content of 50% and, besides buta-
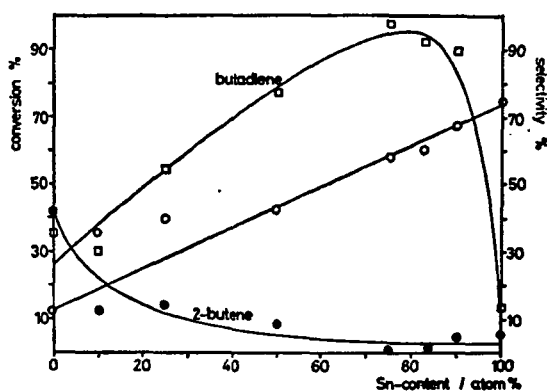

Fig. 1. Conversion and selectivity as a function of catalyst composition in the oxidation of 1-butene.
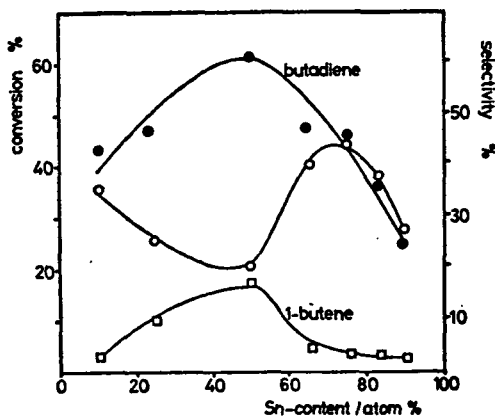

Fig. 2. Conversion and selectivity as a function of catalyst composition in the oxidation of 2-butene

diene, 1-butene is found too. The amounts of 1-butene and 2-butene in the product approximate to their values at thermodynamic equilibrium. The conversion over mixed oxides containing more than 50% tin increases, but the selectivity for buta-diene decreases considerably. The double-bond isomerization similarly decreases.

Conversion and selectivity as a function of reaction temperature

The influence of temperature is illustrated by measurements over the mixed oxide with Sn:Sb=3:1, which was found to be the most effective catalyst in the oxidation of 1-butene.

As expected, the activity of the catalyst (the conversion) in the oxidation of 1-butene (Fig. 3) increases, but the selectivity decreases considerably as the reaction temperature rises. The latter is a consequence of the oxidation of butadiene at higher temperature (673 K).
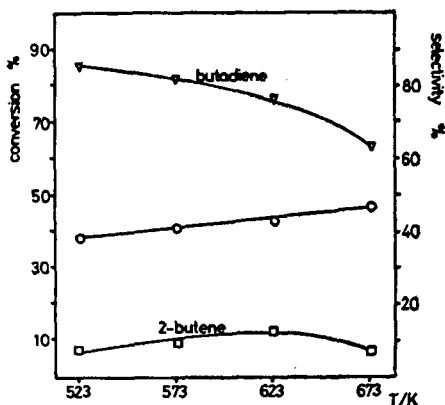

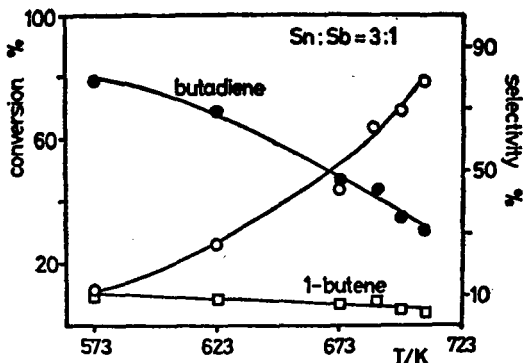*Fig. 3.* Temperature-dependence of 1-butene oxidation over a Sn:Sb=3:1 catalyst

Fig. 4. Temperature-dependence of 2-butene oxidation over a Sn:Sb=3:1 catalyst

The characters of the curves in the oxidation of 2-butene (Fig. 4) are similar, but the conversion and the selectivity are much lower at all reaction temperatures. The selectivity for butadiene is only 40% at 673 K. This can be explained in that the reaction rate of butadiene oxidation is commensurable with the reaction rate of the initial reactant 2-butene. This cannot be found in the oxidation of 1-butene, for 1-butene has a higher reactivity; thus, the amount of active surface oxygen decreases rapidly, and the butadiene cannot be oxidized.

Oxidation of butadiene

The tin-antimony mixed oxides may have a role in the oxidation of butadiene, the product of oxidative dehydrogenation. This can reduce the selectivity of the reaction. The stability of butadiene, *i.e.* its behaviour under the given oxidation conditions, was investigated under the same circumstances as for *n*-butenes. Only the conversions at different reaction temperatures and catalyst compositions are shown in Fig. 5; the nature and the selectivities of the products, *e.g.* furan, maleic
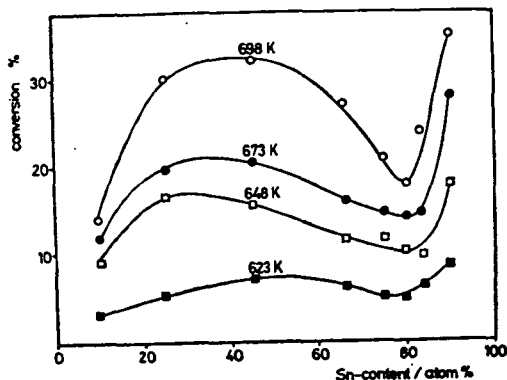
Fig. 5. Conversion as a function of catalyst composition and reaction temperature in the oxidation of butadiene

anhydride, acetaldehyde and mainly CO_2, are independent of the selectivity for butadiene formation in the oxidative dehydrogenation of butenes. Below 623 K, mixed oxides of all compositions are inactive in the oxidation of butadiene. At higher temperatures, the conversion exhibits two maxima as a function of composition, the first at a tin content of 50%, and the second at 90%. This is in accordance with the fact that the optimum catalyst compositions in oxidative dehydrogenation were Sn:Sb=3:1 and 5:1. Over these mixed oxides, 1-butene is oxidized more quickly, but butadiene has a relatively high stability even at 698 K.

Kinetic investigations in a recirculatory flow reactor

Over the mixed oxides with Sn:Sb=3:1 and 5:1, which had been found the best catalysts in previous investigations, the kinetics of oxidation of 1- and 2-butene were studied in the range 573—673 K. The initial mole ratio of the reactants (except in the determination of the order) was $C_4H_8:O_2=1:1$. Results obtained on the oxidation of 1-butene can be seen in Figs. 6—7. Figures 8—9 show the kinetic curves of the oxidation of 2-butene.

Fig. 6. Temperature-dependence of kinetic curves measured in the oxidation of 1-butene over a Sn:Sb=3:1 catalyst

Fig. 7. Temperature-dependence of kinetic curves measuredin the oxidation of 1-butene over a Sn:Sb=5:1 catalyst

At 673 K, the oxidation of 1-butene is a relatively fast reaction. Over both catalysts the half-life of 1-butene is about 100 s. The butadiene formed does not undergo further oxidation until the conversion reaches 90%. At lower temperature, as the half-life of 1-butene decreases, it can be seen that over the mixed oxide with
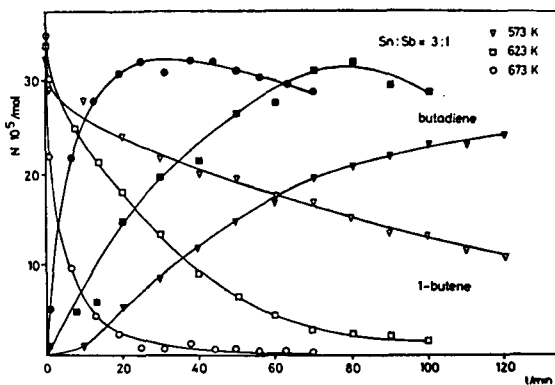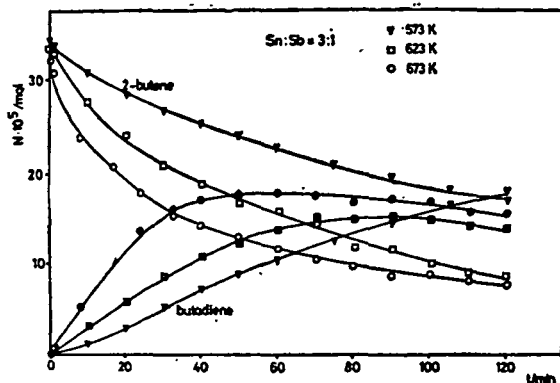
Fig. 8. Temperature-dependence of kinetic curves measured in the oxidation of 2-butene over a Sn:Sb=3:1 catalyst

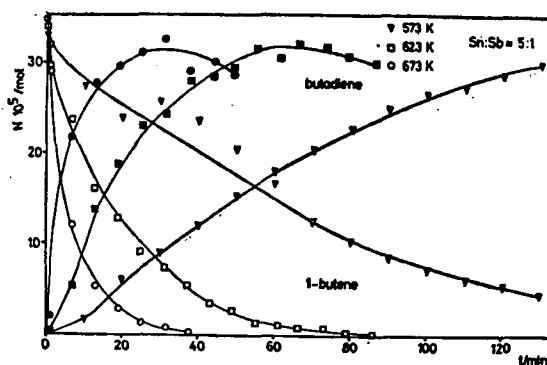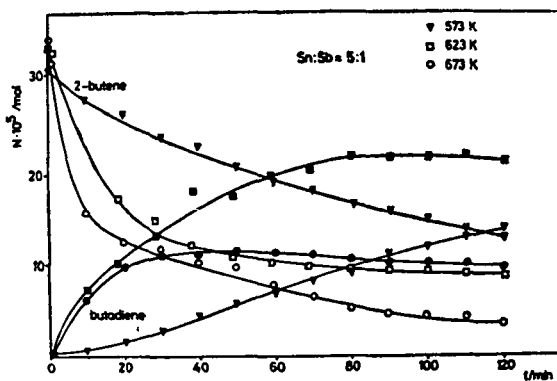*Fig. 9.* Temperature-dependence of kinetic curves measured in the oxidation of 2-butene over a Sn:Sb=5:1 catalyst

Sn:Sb=5:1 the rate of reaction is higher than in the case of Sn:Sb=3:1. At these temperatures (573 K and 673 K) the oxidation of butadiene cannot be observed.

The oxidation of 2-butene is a much slower reaction. The respective rate constants are lower by nearly one order of magnitude. The ratio of the two isomers changes during the reaction: the initial *cis:trans* ratio of 3:1 becomes 2:1 at half-life, and then decreases to 1:1, which shows that *cis*-2-butene is oxidized more quickly.

Previous results of the kinetic investigation of the oxidation of olefins over mixed oxide catalysts showed that the rate of the reaction can be described by the equation [16]:

$$-\frac{dp_{\text{olefin}}}{dt} = k \cdot p_{\text{olefin}}^{n} p_{\text{O}_2}^{m}$$
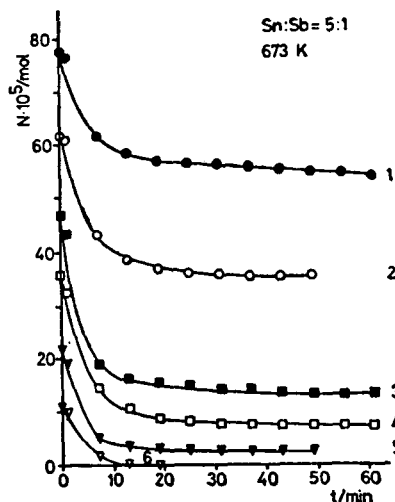
Fig. 10. Determination of partial order for butene. Kinetic curves (the amount of 1-butene as a function of reaction time) determined in the oxidation of 1-butene over a Sn:Sb=5:1 catalyst at a fixed initial partial pressure of O_2=65.8 mbar. Curves 1, 2, 3, 4, 5 and 6 were measured at p^0_{buten}=32.9, 65.8, 98.7, 131.6, 197.4 and 263.2 mbar, respectively

Fig. 11. Determination of partial order for dioxygen. Kinetic curves (the amount of 1-butene as a function of reaction time) determined in the oxidation of 1-butene over a Sn:Sb=3:1 catalyst at a fixed initial partial pressure of 1-butene=65.8 mbar. Curves 1, 2, 3, 4 and 5 were measured at $p^0_{O_2}$=26.3, 32.9, 65.8, 131.6 and 263.2 mbar, respectively

The partial order with respect to 1-butene was determined. From the kinetic curves (Fig. 10) obtained at a constant initial pressure of dioxygen ($p_{O_2}^0$), it was found that $n = 0.92 \pm 0.1$ if $p_{butene}^0 : p_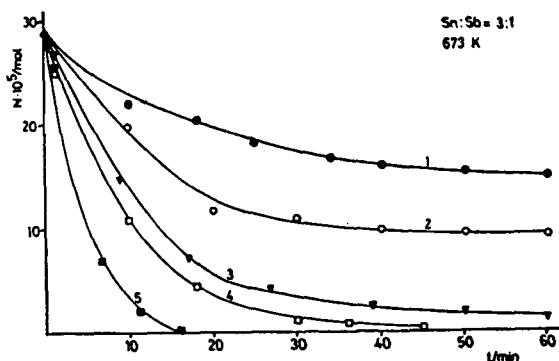{O_2}^0 \leqq 2$. It should be mentioned that a value of $n < 0$ emerges from measurements at $p_{butene}^0 : p_{O_2}^0 > 2$. The order with respect to dioxygen was determined at a constant value of p_{butene}^0 (Fig. 11), which gave $m = 0.55 \pm 0.05$. From this, the rate equation for the oxidation of butene can be approximated to by the relationship:

$$-\frac{dp_{butene}}{dt} = k \cdot p_{butene} p_{O_2}^{0.5}$$

Via the half-lives derived from this equation, the apparent rate constants can be calculated [17] if $p_{butene}^0 = p_{O_2}^0$. Table II lists apparent activation energies and pre-exponential factors determined from the apparent rate constants calculated previously, and their dependence on the reaction temperature.

Table II

Kinetic parameters of oxidation of butanes

Reactant	Catalyst	$T_{reac.}$ K	$t_{1/2}$ s	$k \cdot 10^3$ $mol^{1/2} s^{-1} g^{-1}$	$E^{\neq}$ kJ mol^{-1}	A $mol^{1/2} s^{-1} g^{-1}$
1-butene	Sn:Sb=3:1	573 623 673	4560 1320 150	8.87 30.64 269.7	108.5	5.7×10^7
	Sn:Sb=5:1	573 623 673	3120 900 120	12.96 44.94 337.0	103.6	3.1×10^7
2-butene	Sn:Sb=3:1	573 623 673	7200 3300 960	5.61 12.27 42.13	64.1	3.5×10^3
	Sn:Sb=5:1	573 623 673	6000 2700 720	6.74 14.98 56.2	67.4	8.4×10^3

As concerns the data in Table II, it may be stated that the apparent activation energies and pre-exponential factors obtained for the oxidation of 1-butene correlate well to literature data for mixed tin-antimony oxides of similar composition. The apparent activation energy for the oxidation of 2-butene is lower by approx. 30 kJ mol^{-1} than that found for 1-butene, and the pre-exponential factors differ significantly too.

In an investigation of the reason for the different behaviours of 1-and 2-butene, the double-bond isomerization was studied over the mixed oxide with Sn:Sb=3:1 at 473 K in the absence of dioxygen. The results are to be seen in Fig. 12. For both starting substances, the concentrations (partial pressures) of the reactants reach thermodynamic equilibrium in a short time (less than 15 minutes). The isomerization
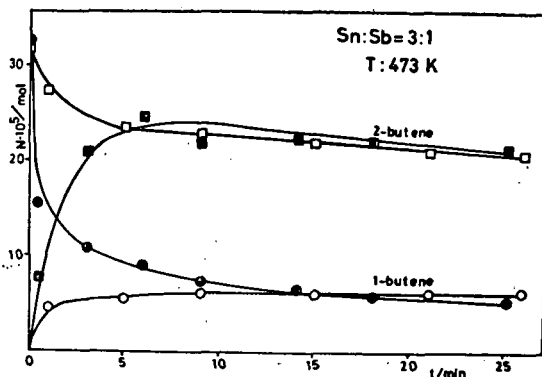
Fig. 12. Kinetic curves of double-bond isomerization of
1-butene (○) to 2-butene (□) and 2-butene (■) to
1-butene (●) over the Sn:Sb=3:1 catalyst at 473 K

can take place in the presence of dioxygen too, but it is a slower reaction than the oxidation of 1-butene. However, the rate of isomerization is probably larger than the rate of oxidation of 2-butene, so it is possible that the oxygen undergoes reaction with adsorbed 1-butene formed in an isomerization step.

Discussion

The pulse reactor measurements show that in the temperature range 523—673 K 1-butene can be converted into butadiene with high selectivity in the mixed oxide composition range $1:1 \leqq SnO_2:Sb_2O_4 \leqq 9:1$. The optimum catalyst composition is Sn:Sb=5:1, but the mixed oxide with Sn:Sb=3:1 also has high activity and selectivity. Over both oxides, the butadiene formed hardly takes part in further oxidation at 623—673 K, which is therefore the optimum range of reaction temperature.

Investigations in a recirculatory flow reactor on the effects of the composition of the reactants demonstrated that an excess of dioxygen increases the rate of reaction and furthers the oxidation of butadiene to only a small extent. However, on increase of the amount of 1-butene, the rate of oxidation decreases as the quantity of reactant reaches the stoichiometric composition (the order becomes negative). $1-C_4H_8:O_2=1:0.75$—2 seems to be the optimum initial reactant composition, so it is expedient to perform the reaction in the presence of an oxygen excess.

Comparison of the oxidation of the two *n*-butenes demonstrates that both the conversion and the selectivity for butadiene are much lower in the oxidation of 2-butene than in the oxidation of 1-butene. In our opinion, this behaviour may be connected with the double-bond isomerization taking place over the Brönsted-type acidic surface sites of the catalyst. The rate of isomerization is maximum over the mixed oxides of the studied system with the highest acidity (40—75% Sn). During the isomerization step, 2-butene converts into 1-butene, which either desorbs and then readsorbs on a surface oxidation site, or migrates to an oxidation site as a surface species which can then yield butadiene *via* the π-allyl intermediate.

Over 623 K, in the oxidation of 2-butene, the butadiene formed takes part in considerable further oxidation, in contrast with that of 1-butene. This different character can be explained by the fact that the active surface oxygen is used up in a fast oxidation of 1-butene, but in the slow reaction of 2-butene butadiene has time to respond to chemisorbed or lattice oxygen, so that the selectivity decreases considerably. The measurements made so far suggest that the oxidative dehydrogenation of butenes over mixed tin-antimony oxides can be described by the following simple scheme:

$$1\text{-butene} \xrightarrow{O_2} \text{butadiene} \xrightarrow{O_2} \left| \begin{array}{l} \text{furan} \\ \text{MSA} \\ \text{methyl ethyl ketone} \\ \text{CO, CO}_2 \end{array} \right.$$

The detailed mechanism found in further investigations will be published in a following paper.

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ИЗУЧЕНИЕ ОКИСЛИТЕЛЬНОЙ ДЕГИДРОГЕНИЗАЦИИ н-БУТЕНОВ НА СМЕШАННЫХ ОЛОВО-СУРЬМЯНЫХ ОКСИДАХ

К. Варга, Я. Галас, К. Гернади и П. Фейеш

Изучено окисление н-бутенов в газовой фазе на смешанных олово-сурьмяных оксидных катализаторах SnO_2—Sb_2O_4 в импульсных и рециркуляционных реакторах в области температур 523—673 K. На катализаторах содержащих более 50% олова введенное количество 1-бутена польностью превращается в бутадиен. Реакция 2-бутена в значительной мере зависит от состава катализатора.