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Partial Oxidation of 1,3-Butadiene on $V_2O_5/Al_2O_3/Al$-Coated Catalysts: Effects of Pore Lengths on Product Selectivities

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Partial oxidation of 1,3-butadiene has been carried out on $V_2O_5/Al_2O_3/Al$-coated catalysts. These catalysts are characterized by uniform pore textures; i.e., the catalysts have unbranched pores, which are vertical to the Al_2O_3 surface. The pore lengths and the pore diameters can be preselected by the method of preparation, but in a given catalyst all pores have the same length and the same diameter. For the present study three catalysts having pore lengths of 75, 11, and 2.5 μm have been used. The pore diameter was in the range of 15 to 20 nm for the three catalysts. The activity for the catalysts is only dependent on the amount of V_2O_5 but independent of the pore lengths. By contrast, the selectivity to the sum of organic products as well as to individual organic products is markedly dependent on the pore length. Products which occur in an early stage of the multistep oxidation reaction are favored by short pores, products which occur in an intermediate stage are favored by intermediate pore lengths, and products which occur in a late stage are favored by long pores.

INTRODUCTION

In consecutive reactions like hydrocarbon oxidations, one of the major goals is to maximize the selectivity to a desired product. Such efforts have led to the development of coated catalysts. Due to the limited coat thickness the diffusion pathways of molecules in such coated catalysts are also limited and, as a consequence, selectivities to desired products could be increased in a number of cases (*1–4*).

The first theoretical treatment of the correlation between pore texture and selectivity in heterogeneously catalyzed consecutive reactions has been advanced by Wheeler, who found that larger pores should lead to higher selectivities (*5*). This has been subsequently confirmed by a number of authors, not only by theoretical considerations but also by correlations between experimental and calculated data (*2, 4, 6, 7*). It is, however, a common feature of all of the previous investigations concerning this problem that the authors utilized characteristic pore lengths which are idealized and cannot reflect the true pore systems. The irregular pore textures of real catalysts encompass different pore diameters, different pore lengths, and more or less branched pore systems. Hence, a rigorous experimental test concerning the effect of the pore diameter and/or pore length of a real catalyst upon the selectivity could not be conducted.

By contrast, it was shown by us in previous work that the anodic oxidation of aluminum wire in aqueous acidic media affords a coated Al_2O_3/Al-species with a regular pore texture. In particular, all pores of a given catalyst have the same lengths, are unbranched, and are vertical to the surface (*8*). More recently, a $V_2O_5/Al_2O_3/Al$-coated catalyst has been prepared by impregnation of such Al_2O_3/Al-species (*9*), and this catalyst has been shown to exhibit high selectivity in the oxidation of 1,3-butadiene (*10*). Since by anodic oxidation of aluminum wire the thickness of the Al_2O_3-coat and, hence, the pore length can be preselected at will within wide boundaries, this catalyst system lends itself ideally to a true test of the correlation between selectivity and pore length.

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In the following we describe the oxidation of 1,3-butadiene on three $V_2O_5/Al_2O_3/$Al-coated catalysts having different pore lengths (Table 1) in an attempt to show possible influences of the pore lengths upon activity and selectivity.

EXPERIMENTAL

Catalysts. By a previously published procedure, three $V_2O_5/Al_2O_3/$Al-coated catalysts have been prepared (*9*). Owing to the specific method of preparation, these catalysts have uniform pore textures and differ only in the pore lengths and in the vanadium content (Table 1).

Catalytic measurements. The oxidation reactions were carried out in a conventional flow apparatus using a fixed-bed reactor. The apparatus and the analytical methods have been described in a previous paper (*9*). In all experiments a constant temperature of 593 K and a constant feed ratio of 0.5 vol% butadiene in air was applied. The space velocities varied in the range of $(1.3–12) \times 10^3\ h^{-1}$ (STP).

RESULTS AND DISCUSSION

Activity measurements. In the first phase of the investigation, the activities of the three $V_2O_5/Al_2O_3/$Al-coated catalysts were determined by measuring the conversion of 1,3-butadiene at constant temperature and a constant ratio of butadiene to air and at changing space velocities. A prerequisite for the application of this method for the comparison of activities is the complete utilization of the entire catalyst in the oxidation reaction, i.e., an effectiveness factor of unity for each catalyst applied. Due to the specific nature of the coated catalysts, the usual criteria for an effectiveness factor of unity, viz., identical conversion levels at the original and the crushed catalyst, could not be applied. Therefore, the following procedure was used for assessing the effectiveness factor: Butadiene was oxidized at the catalyst 1 which has the longest pore length at 593 K and at varying space velocities. Using a space velocity of 1500 h^{-1} (STP) a conversion C of 95% was obtained. On the basis of these experimental data, the rate constant k of the reaction was calculated to 4.6 s^{-1} by Eq. (1) and by assuming a first-order reaction:

$$\ln \frac{1}{1 - C} = k \cdot t. \qquad (1)$$

Using the above value for k and an effective diffusion coefficient D_{eff} of 0.2 cm s^{-2}, a Thiele modulus φ of 0.12 and an effectiveness factor η of 0.99 (Eq. (2)) were calculated for a rod-shaped bulk catalyst having the same dimensions as the three $V_2O_5/Al_2O_3/$Al-coated catalysts applied in this study:

$$\eta = \frac{\tanh \varphi}{\varphi} \qquad (2)$$

It was concluded from these results that the coated catalysts have effectiveness factors of unity, since their pores are 10 to 10^2 times shorter than the characteristic length of the bulk catalyst upon which the calculation of the effectiveness factor has been based.

The above results show that the prerequisites for a comparative study of the activities of the three $V_2O_5/Al_2O_3/$Al-coated catalysts 1–3 were fulfilled. Therefore, the activities of the three $V_2O_5/Al_2O_3/$Al-coated catalysts have been determined. Figure 1 shows plots of conversion vs the modified residence time τ_m ($\tau_m = W/F$) at a constant

TABLE 1

Data of $V_2O_5/Al_2O_3/$Al-Coated Catalysts[a] (*9*)

Catalyst	Pore length (μm)	Specific surface area (BET) (m^2/g)	Average vanadium content[b] (wt%)
1	75	3.46	2
2	11	0.82	4
3	2.5	0.13	3[c]

[a] Pore diameters: 15–20 nm.
[b] Related to the mass of alumina.
[c] Maximum value.

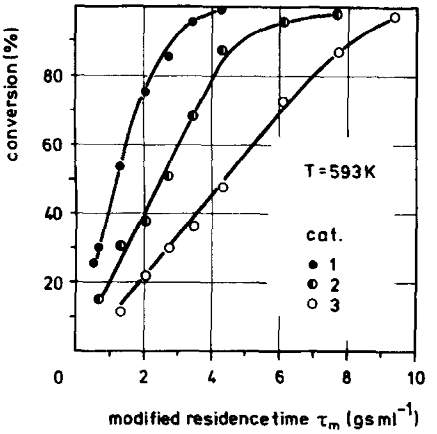


FIG. 1. Conversion vs modified residence time τ_m in the oxidation of 1,3-butadiene on $V_2O_5/Al_2O_3/Al$-coated catalysts; pore lengths: 75 μm (cat. 1), 11 μm (cat. 2), 2.5 μm (cat. 3).

temperature at 593 K. As expected, the conversion increased for each catalyst with increasing residence time. Furthermore, there were marked differences between the activities of the three catalysts in the sequence cat. 1 > cat. 2 > cat. 3; i.e., the catalyst with the largest pores showed the highest activity, and the catalyst with the shortest pores showed the lowest activity. A priori, these differences in activity could have been caused by different specific surface areas and/or by different average vanadium content and/or different ratios of catalytic active vanadium surface area to mass of vanadium of the three catalysts. In order to identify the true cause(s), the differences in the BET surface among the three catalysts were eliminated by plotting the butadiene conversion vs the modified residence time τ_a, which is obtained by multiplying τ_m by the BET surface areas of the individual catalysts. This resulted in the curves depicted in the Fig. 2. Evidently, the activity sequence of the catalyst is now reversed to cat. 3 > cat. 2 > cat. 1; i.e., the catalyst with the shortest pores shows the highest activity and the catalyst with the longest pores shows the lowest activity. A priori, this could be caused by different average vanadium content and/or by different ratios of catalytically active vanadium surface area to mass of vanadium in the three catalysts. In order to differentiate between these causes, the differences in the average vanadium content were eliminated by plotting the butadiene conversion vs the modified residence time τ_v, which is obtained by multiplying τ_a by the specific vanadium content of the individual catalysts. The specific vanadium content of a catalyst is obtained by multiplying its average vanadium content by the mass of Al_2O_3 and dividing the product by the BET surface area. Since the vanadium contents were determined by microprobe analyses, average values could

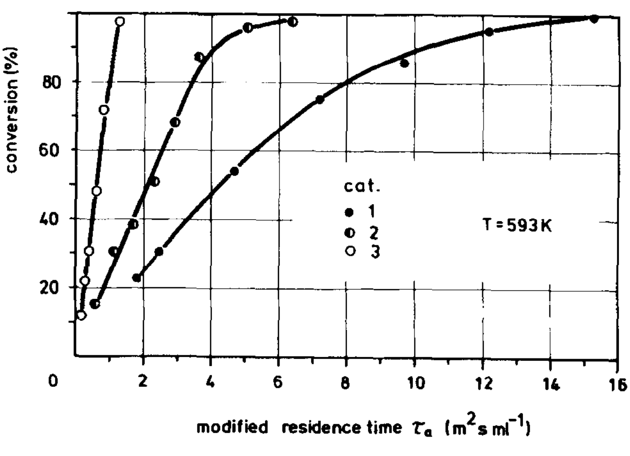


FIG. 2. Conversion vs modified residence time τ_a in the oxidation of 1,3-butadiene on $V_2O_5/Al_2O_3/Al$-coated catalysts; pore lengths: 75 μm (cat. 1), 11 μm (cat. 2), 2.5 μm (cat. 3).

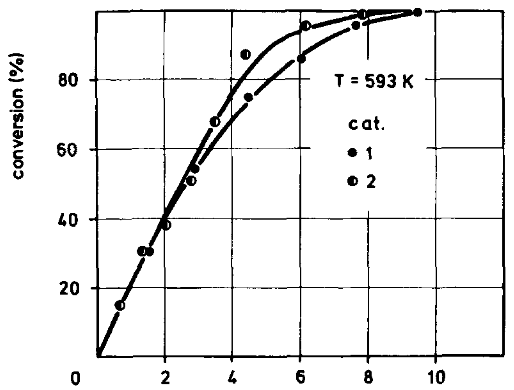


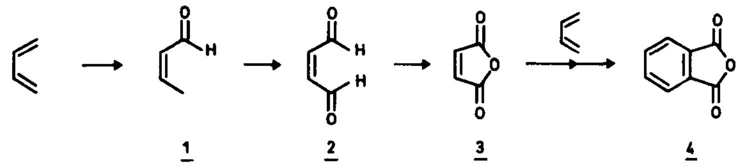
FIG. 3. Conversion vs modified residence time τ_v (s ml^{-1}) in the oxidation of 1,3-butadiene on V_2O_5/Al_2O_3/Al-coated catalysts; pore lengths: 75 μm (cat. 1), 11 μm (cat. 2).

only be obtained for catalysts 1 and 2, which have intermediate and large Al_2O_3 coats, whereas analysis of catalyst 3 gave only a maximum, but no average value. As a consequence, τ_v values could only be reliably calculated for catalysts 1 and 2; they amounted to 0.62 and 1.22 m^{-2}, respectively.

Figure 3 shows the correlation between conversion and modified residence time τ_v for catalysts 1 and 2. It is obvious that the two curves coincide completely up to a conversion of 60% and that they nearly coincide at conversions between 60 and 100%. It is concluded from this result that the ratio of the catalytically active vanadium surface area to the mass of vanadium is nearly identical for the two catalysts. It can be further concluded that the activity of the catalysts is only dependent on the vanadium content, which is related to the modified residence time τ_v.

Selectivity measurements. In the second phase of the investigation, the selectivities to the sum of organic products and to essential individual organic products at the three catalysts have been determined.

Figure 4 shows a plot of the overall selectivity to organic products vs conversion. It is evident that over the entire range of conversions the selectivity sequence is cat. 3 > cat. 2 > cat. 1; i.e., the catalyst with the shortest pores provides the highest selectivity, and the catalyst with the longest pores provides the lowest selectivity. Furthermore, the selectivities decrease moderately with increasing conversions in the range of 15 to 90% and considerably at conversions above 90%. Crotonaldehyde (**1**), butenedial (**2**), maleic anhydride (**3**), and phthalic anhydride (**4**) have been selected for the measurement of the selectivity of individual organic products, because it had been shown in a preceding study, that the former two compounds are the single most important intermediate and the latter two compounds are the only essential final organic products (*9*). On the basis of these previous results, the oxidation of 1,3-butadiene was assumed to proceed by the following reaction sequence:



SCHEME I

Figure 5 shows the selectivities for products **1** to **4** vs conversion in the oxidation on the three different catalysts. It is evident that the selectivities to these products experience different influences from the catalyst pore lengths. Apparently, the selectivity to crotonaldehyde (**1**) is not influenced by the pore lengths and the selectivity drops with increasing conversion from approximately 8% to nearly 0% for the three

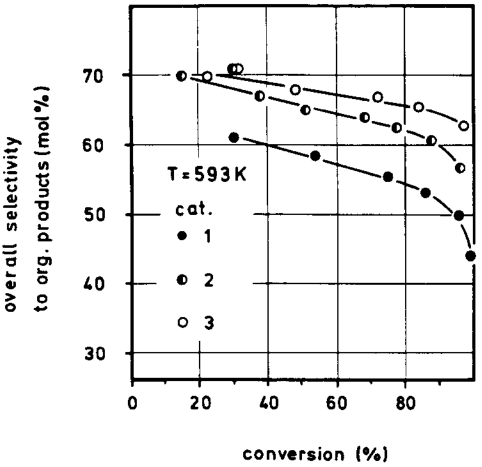


FIG. 4. Overall selectivity to organic products vs conversion in the oxidation of 1,3-butadiene on $V_2O_5/Al_2O_3/Al$-coated catalysts; pore lengths: 75 μm (cat. 1), 11 μm (cat. 2) and 2.5 μm (cat. 3).

catalysts. By contrast, the selectivity to butenedial (**2**) is markedly influenced by the catalyst pore lengths in the sequence cat. 3 > cat. 2 > cat. 1; i.e., the catalyst with the shortest pores provides the highest selectivity, and the catalyst with the longest pores provides the lowest selectivity. Furthermore, all selectivity curves exhibit maxima at low conversions of ca. 30%. The selectivity curves for maleic anhydride (**3**) show a different behavior. In this case, the selectivity sequence is cat. 2 > cat. 3 > cat. 1; i.e., the catalyst with the intermediate pore length provides the highest selectivity, whereas both the catalyst with the shortest and the one with the longest pores provide lower selectivities. Furthermore, the selectivities increase for all catalysts over the entire range of conversions from 15 to ca. 90% and show a moderate decrease at conversions above 90%. Finally, the selectivities to phthalic anhydride (**4**) are also dependent on the catalyst pore lengths. In contrast to maleic anhydride, however, the selectivity sequence is cat. 1 > cat. 2 > cat. 3; i.e., the catalyst with the longest pores provides the highest selectivity, and the catalyst with the shortest pores provides the lowest selectivity. Furthermore, the selectivity curves show a decline toward higher conversions and the curve for catalyst 1 shows a maximum value at approximately 40% conversion.

An attempt at explaining the above experimental results has been made by the following considerations: Due to our unique catalyst system, which has pores of uniform lengths, the characteristic length L in the Thiele equation can now be substituted by the real pore length lp. Furthermore, since the effectiveness factor has been determined to be $\eta = 1$, the Thiele modulus must be $\varphi \leq 1$. These considerations lead to a modified Thiele Eq. (3) and to its square, Eq. (4),

$$\varphi = \mathrm{lp}\sqrt{\frac{k}{D_{\mathrm{eff}}}} \leq 1 \tag{3}$$

$$\mathrm{lp}^2\,\frac{k}{D_{\mathrm{eff}}} \leq 1. \tag{4}$$

Further modification of Eq. (4) by $\tau_R = k^{-1}$ and $\tau_D = \mathrm{lp}^2 \cdot D_{\mathrm{eff}}^{-1}$ leads to Eq. (5):

$$\frac{\tau_D}{\tau_R} \leq 1. \tag{5}$$

In this equation, τ_D is the time constant of diffusion, which is equal to the probable intrinsic residence time, and τ_R is the time constant of reaction, which is equal to the probable lifetime of a molecule in the catalyst pore (*7*). From the definitions of τ_R and τ_D it follows that for constant reaction conditions, i.e., for k = const and D_{eff} = const, τ_R is constant and τ_D is only dependent on the pore length lp. It can be further concluded, that the pore length lp can vary in the range of the validity of Eq. (5) without a drop of the effectiveness factor. This means that there is no mass transport limitation by pore diffusion and that, hence, different intrinsic residence times result exclusively from different pore lengths.

On the basis of the above considerations we propose the following explanation for the dependence of the product selectivity on the pore length of a consecutive reaction of type A → B → C (Fig. 6).

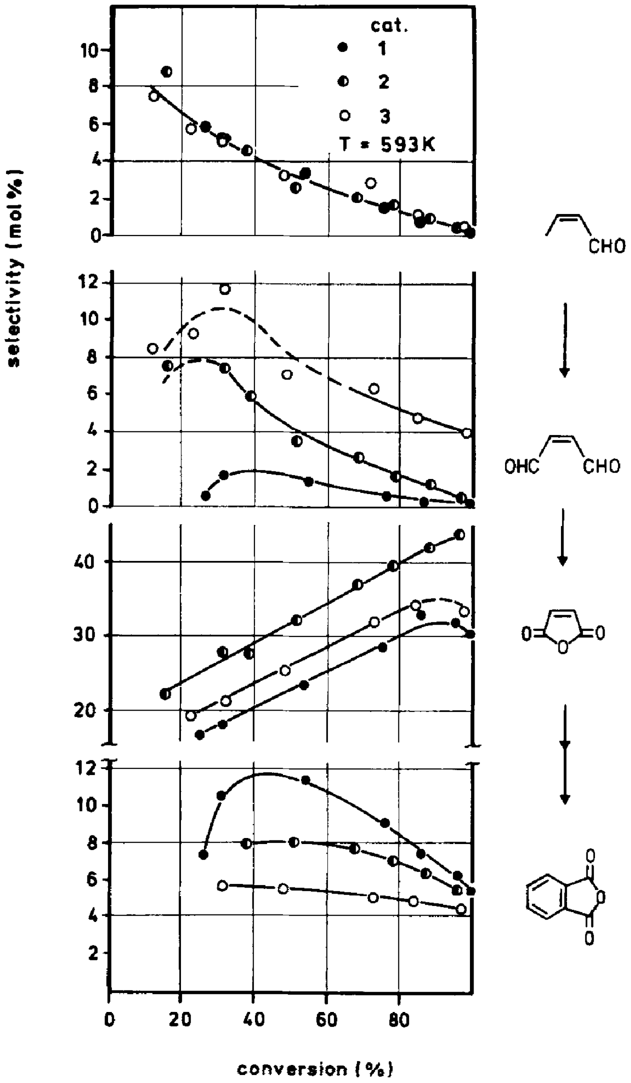


FIG. 5. Product selectivities vs conversion in the oxidation of 1,3-butadiene on $V_2O_5/Al_2O_3/Al$-coated catalysts; pore lengths: 75 μm (cat. 1), 11 μm (cat. 2) and 2.5 μm (cat. 3).

In the first step, substrate A is converted into the intermediate B both in a short pore with the length lp_1 and in a long pore with the length lp_2. In the short pore (lp_1) no further reaction of B takes place due to its limited residence time, which is shorter than the probable lifetime. Therefore, B migrates out of the pore into the gas bulk phase. In the long pore (lp_2), by contrast, intermediate B is converted to the final product C due to the enhanced intrinsic residence time of B, which is now longer than its probable lifetime. This is, of course, an idealized representation of the true situation. For, in real consecutive reactions, such as selective oxidations of hydrocarbons, intermediate B can be also in part converted into C in short pores and, furthermore, there are in most cases several intermediates $B_1, \ldots, B_n$ formed on the way from $A \rightarrow C$.

In the light of the foregoing discussion the correlations between selectivity and pore lengths depicted in Fig. 5 can be ra-

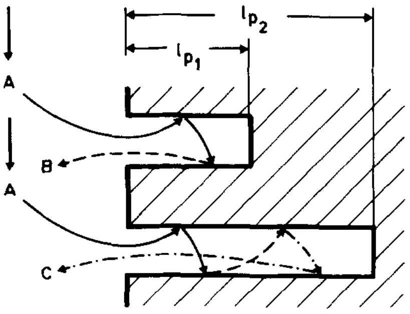


FIG. 6. Schematic representation of consecutive reactions in catalysts of different pore lengths; lp_1, lp_2: pore lengths, A: educt, B: intermediate product, C: final product.

tionalized in the following way: The selectivity to crotonaldehyde as the primarily formed product is independent of the pore length, possibly due to the uniform and relatively high concentration of the substrate butadiene in the pores of any length. The selectivity to butenedial reaches maximum values at the catalyst, having the shortest pores, since in this case a relatively high proportion of butenedial leaves the pore prior to further oxidation. Conversely, the selectivity to butenedial in the catalysts with longer pores decreases due to enhanced further oxidation to maleic anhydride. The selectivity to maleic anhydride reaches maximum values at the catalyst having an intermediate pore length, since at the catalyst with the shortest pores a considerable part of the precursor butenedial leaves the catalyst prior to further oxidation and since at the catalyst with the longest pores a considerable part of maleic anhydride undergoes subsequent reaction with butadiene to give phthalic anhydride. The selectivity to phthalic anhydride, finally, reaches maximum values at the catalyst having the longest pores, due to the extended intrinsic residence times, which are necessary for this multistep reaction.

In summary, the present investigation has shown that in the oxidation of 1,3-butadiene the overall selectivity to organic products is markedly influenced by the catalyst pore length. It appears, furthermore, that there exists an optimum pore length for the selective formation of individual organic products in the sense that, in the multistep oxidation of butadiene, products which occur early in the reaction sequence are favored by short pores, products which occur in the middle of the reaction sequence are formed by pores of intermediate lengths, and products which occur at the end of the reaction sequence are favored by long pores.

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