

Partial Oxidation of 1,3-Butadiene on $V_2O_5/Al_2O_3/Al$ -Coated Catalysts: Products and Reaction Routes

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Partial oxidation of 1,3-butadiene has been investigated on $V_2O_5/Al_2O_3/Al$ -coated catalysts having regular pore textures. The preparation of the coated catalysts by means of anodic oxidation of aluminum wire and subsequent impregnation of the Al_2O_3 layers is described. The catalysts were characterized by the textural parameters surface area, pore length, and pore diameter as well as by the contents of aluminum, vanadium, and sulfur. The alumina layers possess amorphous structures and regular pore systems, in which the layer thickness corresponds to the pore length. In the oxidation of butadiene a total of 33 organic oxidation products have been identified, including maleic anhydride as the major product and among others phthalic anhydride, crotonaldehyde, and butenedial. The dependence of selectivity on conversion has been determined for products which are crucial for the mode of formation of the major reaction product maleic anhydride. Based on these results, reaction schemes for the formation of maleic anhydride and of phthalic anhydride have been proposed. © 1987 Academic Press, Inc.

INTRODUCTION

Coated catalysts have been used for a long time in industrial organic syntheses, especially in partial oxidation reactions of hydrocarbons. The utilization of such catalysts is advantageous in reactions having high reaction rates. Prominent examples are the formation of maleic anhydride by selective oxidation of benzene or for C_4 hydrocarbons as well as the formation of phthalic anhydride by selective oxidation of *o*-xylene or of naphthalene. Conventional coated catalysts consist of an inert unporous support, e.g., α - Al_2O_3 or SiC, which bears the catalytically active components, e.g., V_2O_5/TiO_2 or MoO_3/V_2O_5 , as shell or coat. Such shells are usually characterized by a thickness of 0.03–2 mm and by an irregular pore system. The major advantages of such coated catalysts are short diffusion pathways which are imparted by the limited thickness of the coat. As a consequence, the selectivity for the formation of organic intermediates is higher than in corresponding reactions catalyzed by bulk catalysts.

Major disadvantages are low adhesion strength of the coat on the support, nonuniform thickness of the coat, and the irregular pore system. These drawbacks provided considerable incentive for the development of new types of coated catalysts (1–11).

Our own efforts in this area of research started out with the preparation of an Al_2O_3/Al -coated material which was prepared by anodic oxidation of an aluminum wire (9). By this method, most of the drawbacks outlined above for conventional catalysts could be overcome: the alumina layer is strongly adhered to the aluminum core and it has a uniform thickness as well as a regular pore system. Furthermore, the textural parameters of the amorphous alumina coat can be preselected within certain boundaries by varying the conditions of the anodic oxidation. It was assumed that these properties provided the potential for the application of such materials as supports for improved coated catalysts, particularly for the selective oxidation of hydrocarbons. This assumption is based on the fact that the uniform pore system allows shorter and

more uniform intrinsic residence times of the organic molecules and should hence lead to improved selectivities for intermediate products. In line with this reasoning, the impregnation of coated $\text{Al}_2\text{O}_3/\text{Al}$ materials with V_2O_5 was attempted in the present investigation. The prepared $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3/\text{Al}$ -coated catalysts were used in the partial oxidation of 1,3-butadiene.

Partial oxidation reaction of 1,3-butadiene on vanadium- and/or molybdenum-containing catalysts have been already reported (12–22). They afford maleic anhydride as the major organic product, along with a number of by-products depending on the level of conversion. Based on the identification of such products several proposals for the mode of formation of maleic anhydride have been advanced (17–22) as will be discussed in more detail in this study. In conclusion, the types and the distribution of products in dependence of the level of conversion are described.

EXPERIMENTAL

Catalyst Preparation

Coated $\text{Al}_2\text{O}_3/\text{Al}$ -material. Three different coated $\text{Al}_2\text{O}_3/\text{Al}$ materials were prepared, starting from aluminum wire (purity >99%) of 1 mm in diameter. The aluminum wire was pretreated and anodically oxidized by a procedure described in a previous paper (9). The electrolyte was 20% sulfuric acid. The anodization was carried out at 18–20°C with 19 V dc current. The anodization times were 180, 25, and 6 min for catalysts 1, 2, and 3, respectively.

Impregnation solution. Seven-tenths of a liter of deionized water was heated to 65–70°C and 52.5 g of NH_4VO_3 was added with stirring. To this solution 97 g of oxalic acid was added in small portions while stirring was continued and the solution turned from its original light yellow color to greenish blue, and to a pH < 1. Subsequently, the solution was cooled to room temperature and the pH was adjusted to 4.5 by the dropwise addition of a 10% aqueous solution of NH_4OH .

$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3/\text{Al}$ -coated catalysts. The freshly anodized aluminum wire was rinsed with deionized water and immediately immersed in the impregnation solution at 70°C. The time of immersion was 30 min for catalysts 1 and 2 and 15 min for catalyst 3. The impregnated $\text{Al}_2\text{O}_3/\text{Al}$ wire was in each case rinsed for 1 min with deionized water, dried at 120°C for 2 h, cut into pieces of 5 mm length, and calcined at 450°C in air for ca. 3 h. It is noteworthy that all attempts at impregnating previously dried $\text{Al}_2\text{O}_3/\text{Al}$ materials with vanadium ions were futile. This means that the generally practiced methods for the preparation of conventional bulk catalysts by impregnation of dry alumina cannot be applied for the preparation of these coated $\text{Al}_2\text{O}_3/\text{Al}$ catalysts.

Measurements of Textural Parameters

Oxide layer thickness. The oxide layer thickness, which corresponds to the pore length, was measured on single catalyst pieces which were enclosed in a casting resin (Palatal/BASF). The measurements were carried out with a optical light microscope for catalysts 1 and 2 and with a scanning electron microscope (Stereoscan Mark II A, Cambridge Instruments) for catalyst 3.

Pore diameter. The pore diameter was obtained by transmission electron microscopy (Hitachi Stereoscan 2000). The measurements were carried out on Al_2O_3 foils, which were prepared under the same conditions of anodization as the three coated catalysts. The procedure has been previously described (9).

Specific surface area. The specific surface areas were obtained by applying the BET method (Micromeritics Accusorb 2100 E) to the adsorption isotherm of krypton at 77 K. Prior to measurement, the catalysts were heated in flowing nitrogen at 300°C for 5 h. Due to the relatively small proportions of the Al_2O_3 shells as compared to the entire $\text{Al}_2\text{O}_3/\text{Al}$ species, the surface areas based on the total mass of the catalysts were relatively low. Hence, catalyst sam-

ples of ca. 20 g were required to get reliable results in the above measurements.

Amount and distribution of Al, S, and V. The amount and the macro distribution of the elements Al, S, and V in the oxide layer were obtained by the line-scan and by the area-scan methods using an electron probe microanalyzer (Jeol JXA 50A). The measurements were carried out on single catalyst pieces enclosed in casting resin as described above.

Oxidation of 1,3-Butadiene

Reactor system and oxidation procedure.

The oxidation of 1,3-butadiene was carried out in a conventional flow apparatus at near atmospheric total pressure. The fixed-bed reactor consisted of a glass tube, having 19 mm i.d. and 40 cm of length. It was immersed in a fluidized bed heat exchanger. A movable thermocouple immersed in the catalyst bed was used to monitor the reactor temperature, which was controlled at better than ± 0.5 K along the entire reactor length. Approximately 20 g of catalyst was loaded into the reactor. The catalyst bed was enclosed by sections of quartz particles. Catalyst activation was carried out with air at 593 K for at least 5 h. Then the reaction mixture, consisting of 0.5 vol% of 1,3-butadiene in air, was introduced into the system and the catalyst was pretreated at 593 K for about 6 h. Subsequently, the actual oxidation reaction was carried out at the same temperature and at space velocities varying in the range of $(1.3\text{--}24) \times 10^3 \text{ h}^{-1}$ (STP). The effluent gas from the reactor was divided into two parts. The major part of the effluent gas was sequentially passed through four traps, of which the first one was cooled to 0°C and the remaining three each to -78°C . The minor part of the effluent gas was analyzed by on-line gas chromatography, using the following conditions: glass column, 2.3 mm \times 2.5 m, packed with 2.5% nitrile silicone oil XE 60 on chromosorb G, 50°C for 10 min, then 50–190°C at 7 K min^{-1} ; nitrogen as carrier gas; flame ionization detector. The condensed

products were collected, separated from the coproduced water with an ultracentrifuge, dried over molecular sieve 4 Å, and analyzed by gas chromatography, using the following conditions: fused silica capillary column, 0.23 mm \times 50 m, silicone oil SE 54, 50°C for 10 min, then 50–180°C at 7 K min^{-1} ; nitrogen as carrier gas; flame ionization detector. For the assessment of the inorganic products CO and CO₂, the effluent gas from a trap kept at 0°C was intermittently passed through an IR photometer, and CO and CO₂ were determined by on-line analysis. The selectivity/yield of a particular product was defined as mole percentage selectivity/yield on a carbon account for basis.

Identification methods. Product identification for each substance was by GC/MS analysis and, except for butenedial, by comparison of retention times with those of authentic samples. In addition, substances which are crucial for recognizing the course of the reaction were isolated by preparative gas chromatography and subsequently identified by ¹H NMR analysis.

RESULTS AND DISCUSSION

Catalyst Characterization

The measured textural parameters of the prepared V₂O₅/Al₂O₃/Al-coated catalysts are summarized in Table 1. Furthermore, the wt-proportions of the elements Al, S, and V based on the weight of the oxide layer are listed. The attained pore lengths were 75, 11, and 2.5 μm for catalyst 1, 2, and 3, respectively; therefore, the ratio of the pore lengths in the three catalysts was 30:4.4:1. The ratio based on the specific surface areas of the three catalysts, viz., 3.46, 0.82, and 0.13 m²/g, should give the same result, due to the uniform pore formation. The calculated ratio was 26.6:6.3:1, which is in good agreement with that obtained on the basis of the measured pore lengths. The measured surface areas are related to the total mass of the catalyst particles, and have, therefore, very low values

TABLE 1

 Textural Parameters and wt-proportions of Al, S, and V of $V_2O_5/Al_2O_3/Al$ -Coated Catalysts^a

Textural parameters and wt-proportions of Al, S and V	Catalyst No.			
	1	2	3	
Layer thickness = pore length	[μm]	75	11	2.5
Surface area ^b BET	[$\text{m}^2 \text{g}^{-1}$]	3.46	0.82	0.13
Average content x of elements ^c	x_{Al}	35	35	—
	x_V	2	4	3 ^d
	x_S	3	2	2.2 ^d

^a Pore diameters: 15–20 nm.

^b Related to the entire catalyst including the metallic core.

^c Related to the alumina layer only.

^d Maximum value.

in the range of 0.1 to 3.5 m^2/g . By contrast, the specific surface areas related to the alumina layer alone were in the range of 35 to about 100 m^2/g . The measured content of elements is related to the alumina layer only. The values for the contents of vanadium and sulfur of catalyst 3 could not be determined reproducibly, because of the small alumina layer thickness. Thus, only maximum values could be obtained for catalyst 3. Figure 1 shows both line scans and area scans from the determination of the contents of Al, S, and V in the alumina layer of catalyst 2. Aluminum is evenly distributed over the total layer thickness and is present at about 35 wt%. Sulfur, which is incorporated into the oxide layer during the anodic oxidation in sulfuric acid, is enriched to about 2 wt% at the interior of the oxide layer. This sulfur content drops rather continuously from the middle of the oxide layer to the outer surface. The content of vanadium, by contrast, increased from about 3 wt% at the border between aluminum and alumina to 5 wt% at the outer surface of the oxide layer. This concentration profile cannot be changed by variation of the impregnation procedure. Thus, it remains the same by changing the duration of impregnation between 15 min and 24 h, by addition of tensides, and by variation of the temperature between 20 and 80°C.

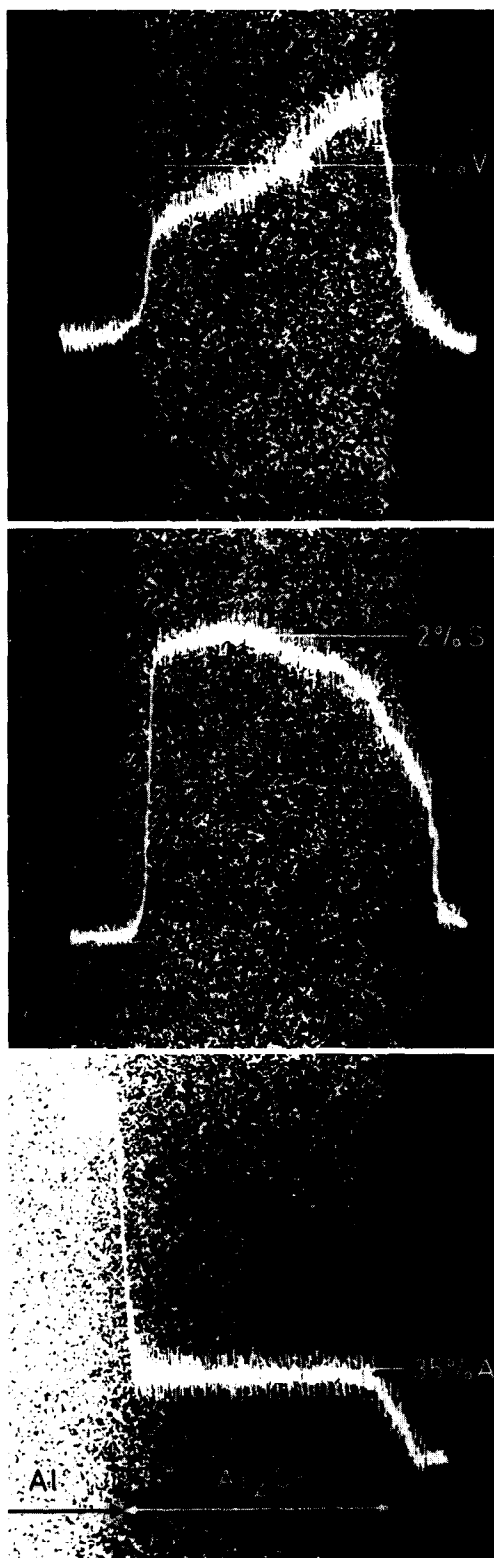


FIG. 1. Content of Al, S and V (line/area scan EPMA) in the oxide layer of catalyst 2.

Oxidation of 1,3-Butadiene

Partial oxidations of 1,3-butadiene on the three coated catalysts were investigated at a constant reaction temperature of 593 K and at conversion levels between 5 and 96%. The latter were realized by varying the space velocities in the range of $(1.3\text{--}24) \times 10^3 \text{ h}^{-1}$ (STP). The selectivity for the formation of organic products on catalyst 2 amounted to 70% at a conversion of 15% and dropped to 56% at a conversion of 96% (Fig. 2). The overall product selectivities obtained on the three coated catalysts 1, 2, and 3 will be given in a subsequent paper

(23). A total of 33 organic products were detected at low and intermediate conversion levels. They were identified as compounds **1a-d**, **2a-c**, **3a**, **3b**, **4a-d**, **5a-g**, **6a**, **b**, **7a**, **b**, **8a**, **b**, and **9-15**. By contrast, only 10 products, viz. **1a-d**, **2a-c**, **3a**, **4a**, and **9**, have been detected at a conversion of 96%. The major organic products at a conversion of 15% were the acyclic oxygenated compounds **1a-d** and **9**, the oxygen-containing heterocyclic 5-membered rings **2a-c** and **3a**, among which maleic anhydride (**2a**) was predominant, as well as the bicyclic phthalic anhydride (**4a**). These products were formed in an overall selectivity of about

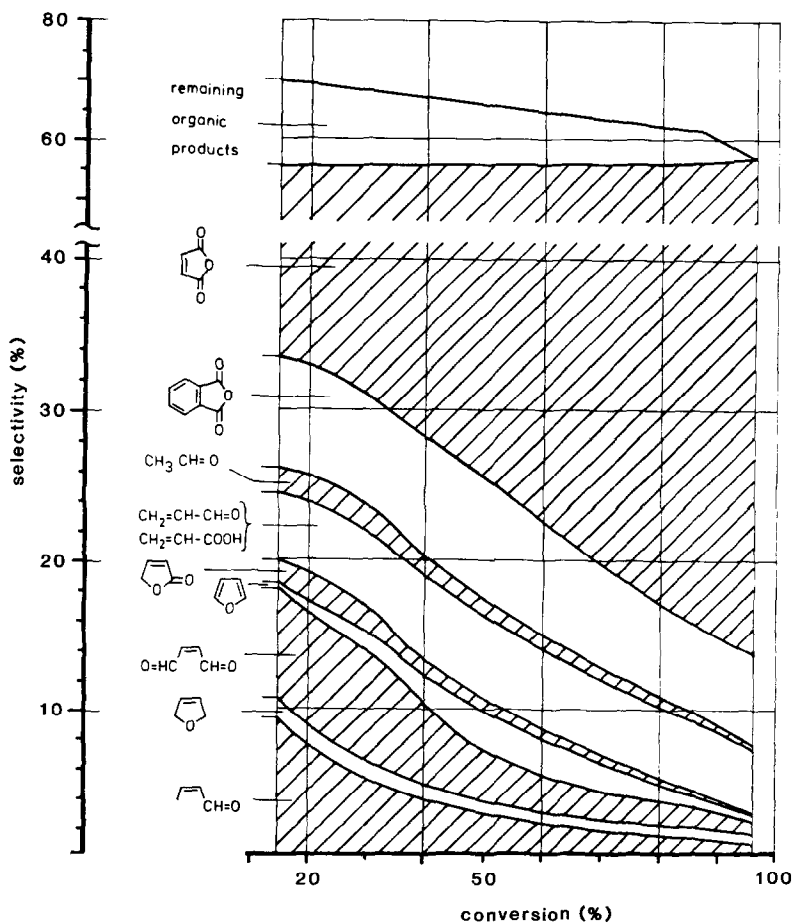
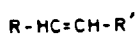
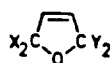


FIG. 2. Selectivity distribution of organic products vs conversion in the oxidation of 1,3-butadiene on the $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3/\text{Al}$ -coated catalyst 2.


1

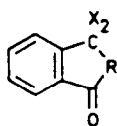
	a	b	c	d
R	CH ₃	CH=O	H	H
R'	CH=O	CH=O	CH=O	COOH


2

	a	b	c
X ₂	O	H ₂	H ₂
Y ₂	O	H ₂	O


3

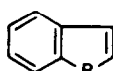
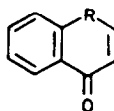
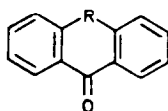
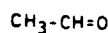
	a	b
R	H	CH=O


4

	a	b	c	d
X ₂	O	O	H ₂	H ₂
R	O	CH ₂	CH ₂	O

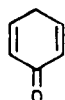
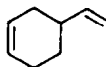
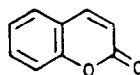
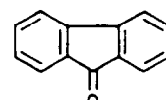

5

	a	b	c	d	e	f	g
R	CH=O	COOH	C ₂ H ₃	C ₂ H ₅	$\begin{matrix} \text{C} \\ \parallel \\ \text{O} \end{matrix}$ CH ₃	$\begin{matrix} \text{C} \\ \parallel \\ \text{O} \end{matrix}$	CH=O
R'	H	H	H	H	H	H	CH=O


6

7

8

9

10

	a	b
R	O	C=O


11

12

13

14

15

56%, whereas the remaining 23 organic products were only formed in an overall selectivity of about 14% and in individual selectivities of less than 1% each.

As can be seen from Fig. 2 there are three different types of products. The first type is maleic anhydride (2a), whose selectivity increased from 23% at 15% conversion to

41% at 96% conversion. The reason for this is probably the fact that V_2O_5 itself has an extremely low activity for maleic anhydride oxidation (15). The second type of products includes phthalic anhydride (4a), acrolein (1c), and acrylic acid (1d) whose selectivities remained approximately constant over the entire range of conversions, e.g., ca. 7% for phthalic anhydride. The third type of products includes crotonaldehyde (1a), butenedial (1b), acetaldehyde (9), furane (3a), 2,5-dihydrofuran (2b), 2-butene-1,4-olide (2c), and the remaining minor organic products 3b, 4b-d, 5a-g, 6a, b, 7a, b, 8a, b, and 10-15. Their overall selectivities decreased from 35% at 15% conversion to 4% at 96% conversion.

In previous investigations of the heterogeneously catalyzed oxidation of butadiene, only 10 of the 33 organic products detected in the present work had been reported. They were 1a-d, 2a-c, 3a, 9, and 13. Prominent among the oxidation products which have been identified for the first time in this study are butenedial (1b) and phthalic anhydride (4a). It is true that butenedial had been invoked previously as an intermediate in a speculative mechanism; however, the authors provided no evidence for the presence of butenedial as a reaction product (24).

For the mode of formation of the single major reaction product maleic anhydride reaction schemes have been repeatedly discussed in the literature (17-22).

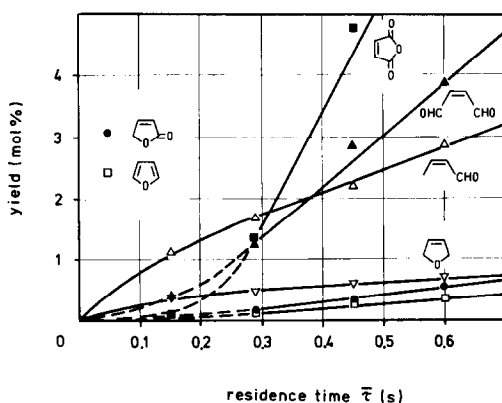
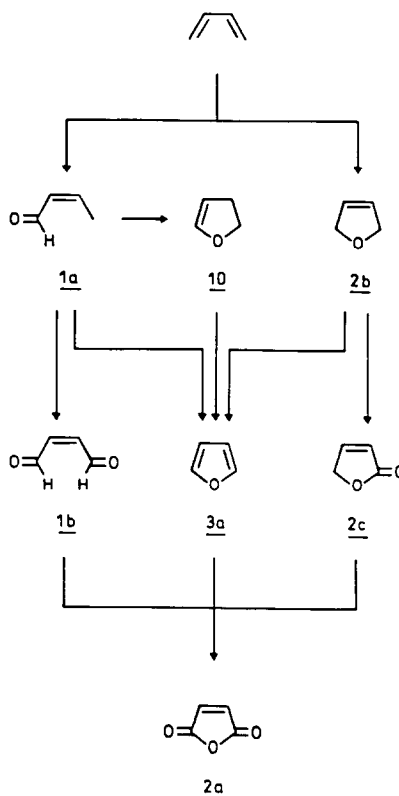
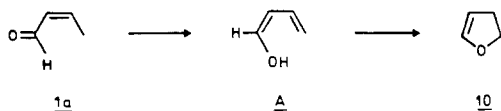


FIG. 3. Yields of some intermediates vs residence time in the oxidation of 1,3-butadiene on the $V_2O_5/Al_2O_3/Al$ -coated catalyst 2.

Most authors have assumed crotonaldehyde (1a) as the primary reaction product which is subsequently converted into 2a via 3a. In some cases 2b has been assumed as the primary reaction product, which is also converted to 2a via 3a (17, 19, 25). In the present study we have identified both 1a and 2b as primary oxidation products as evidenced in Fig. 3 in the oxidation of 1,3-butadiene at low conversions between 5 and 25%.

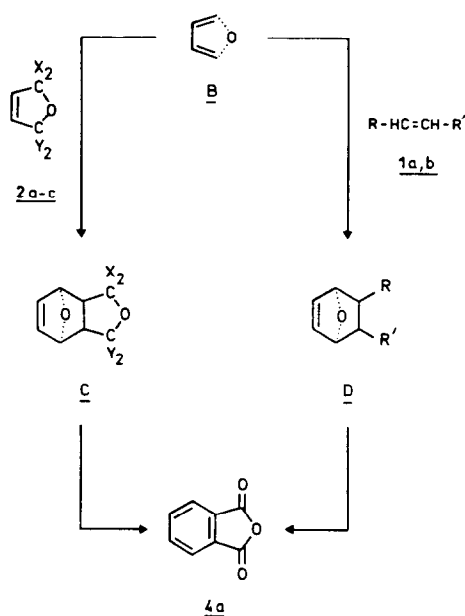
Furthermore, the results of the present investigation suggest that furane (3a) is not the sole secondary product, but that there are also other intermediates on the pathway from the primary products 1a and 2b to the

final product maleic anhydride (**2a**). A consideration of product balances on the basis of Fig. 2 shows that butenedial (**1b**) must and **2c** as well as **10** may contribute to the formation of maleic anhydride. Based on these results we propose now an extended reaction scheme for the formation of maleic anhydride from butadiene. According to this scheme **2b** can react to **2a** via **2c** in addition to the reaction path **2b**–**3a**–**2a** which had been previously described. On the other hand, **1a** can react to form **2a** via **1b** or via **10** and **3a** in addition to the previously proposed route **1a**–**3a**–**2a**. The formation of **10** can be envisioned by enolization of **1a** to give A, followed by intramolecular cycloaddition of the latter.



The formation of phthalic anhydride, which had not previously been recognized as an oxidation product of butadiene, occurs by Diels–Alder additions as the first reaction step. Diene components can be butadiene or furane as indicated by formula B. Monoene components can be the activated cyclic olefins **2a**–**c** to give compounds of type C or the acyclic activated olefins **1a** and **b** to give compounds of type D. In the further course of the oxidation reaction, intermediates C and D are converted into the thermodynamically more stable phthalic anhydride (**4a**).

Of the minor reaction products, compounds **4d**, **5a**, **5b**, **5g**, **6a**, and **14** can be readily explained by Diels–Alder reactions of butadiene with **2c**, **1c**, **1d**, **1b**, **3a**, and **11**, respectively, followed by oxidative aromatization. Furthermore, compound **13** can be explained by Diels–Alder dimerization of butadiene, compound **5c** by aromatization of **13**, and compounds **5d** and **5e** by subsequent reaction of **5c**. For the remaining minor reaction products no proposal concerning the mode of formation can be made.



A notable feature of the present investigation is the large number of products which are formed at low conversion levels. It is believed that this is due to the uniform texture of the $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3/\text{Al}$ -coated catalyst system. The unbranched short pores of uniform pore lengths allow a rapid transport of intermediates into the bulk gas phase. It appeared, therefore, intriguing to test whether the selectivity of individual products can be influenced by variation of the texture of the catalysts, in particular of the pore lengths, and hence by variation of the intrinsic residence times. The results of this study will be reported in a subsequent paper (23).

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