

EFFECT OF VARIOUS MODIFYING ELEMENTS ON THE CATALYTIC PROPERTIES OF VANADIUM-PHOSPHORUS CATALYSTS IN OXIDATION OF BUTANE

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The flow-through method was applied to a study of the catalytic properties of vanadium-phosphorus catalysts ($V : P = 1 : 1.2$) prepared by the method of interaction of H_3PO_4 with V_2O_5 solution in HCl to which a Li, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pd, Cd, Sn, or Ce salt was added as a modifying substance. The catalysts were ordered in a sequence according to the selectivity found in oxidation of butane. Catalysts with modifying elements whose ions possess an incomplete outer electron shell exhibit higher selectivity and yields of maleic anhydride than those in which the introduced ions possess a complete outer electron shell.

The number of scientific and patent publications dealing with selective heterogeneous oxidation of butane to maleic acid has recently grown considerably. Interest in this reaction has obviously been stimulated by two aspects. Until recently, heterogeneous oxidation of alkanes, unlike that of olefins and aromatic compounds, was assumed to result in practically no other products than carbon monoxide and carbon dioxide¹. Recent data, however, do not confirm this concept, indicating that the reaction gives rise to a high quantity of products of incomplete oxidation, particularly maleic anhydride²⁻⁶. Synthesis of this compound by heterogeneous oxidation of butane is of interest also from the economic point of view, as butane is a less expensive raw material than the alternative butenes or benzene.

Efficient catalysts for selective oxidation of butene to maleic anhydride are vanadium-phosphorus catalysts⁶⁻¹¹. These contacts frequently contain additions of other elements stimulating a better catalytic effect of the basic matter. However, the hitherto published data on the properties of such catalysts are not sufficient to enable relations between their composition, structure, and the catalytic effect to be established. For this reason, new catalysts are still being developed empirically.

In the present work, vanadium-phosphorus catalysts have been prepared, each containing one additional modifying element, and their catalytic properties in oxidation of butane were studied with the aim to find relations between the nature of the element added and the catalytic properties of the contact under study.

EXPERIMENTAL

The catalysts were prepared by allowing H_3PO_4 to react with V_2O_5 solution in HCl, containing in addition a salt of the element tested with a nonoxidable anion. After evaporation to dryness, the mass was calcinated on air and treated with an inert gas and a mixture of aliphatic

hydrocarbon with air. Similar methods have been published^{5,7}. V_2O_5 , H_3PO_4 , and HCl were reagent grade purity.

The specific surface area of the catalysts after catalytic activity measurements was determined using gas chromatographic technique by the method of thermal desorption of argon.

The catalytic activity was measured on a flow-through apparatus. The reactor consisted of a quartz tube 0.7 m long, inner diameter 7 mm, packed alternatively with thin layers of the catalyst (grains 0.63–1 mm) and ground silica. A specially designed furnace¹² was used for heating the reactor and ensuring constant temperature along the catalyst bed. Experiments were performed to examine the effect of changes in the linear flow rate of the reacting mixture and the catalyst grain size on the degree of conversion of butane; the temperature of the upper catalyst layers was controlled. No facts were established that would indicate any effect of the macro-physical parameters on the course of the reaction. The possibility was also tested of conducting the reaction on passing the starting mixture through the reactor packed with ground silica and heated to 400–520°C, but no conversion of butane could be traced under such conditions.

Analysis. The starting mixture (1% vol. butane in air) and the reaction products were analyzed gas chromatographically using two Chrom-4 instruments. One of them, fitted with a flame ionization detector, was employed for the determination of hydrocarbons, maleic anhydride, acids, and aldehydes (column 1.2 m long packed with Porapak Q, grain size 100–120 mesh; thermostat temperature 190°C, nitrogen flow rate 0.66 cm³ s⁻¹). On the first column of the other chromatograph (length 1.2 m, packing: Porapak R, grain size 60–80 mesh; thermostat temperature 50°C, carrier gas — hydrogen — flow rate 0.66 cm³ s⁻¹), carbon dioxide was determined by means of a katharometer, while on the second column (length 1.2 m, packing: molecular sieve 5A, grain size 40–60 mesh) carbon monoxide was separated from oxygen and nitrogen. Samples for analysis were taken in capillaries of accurately known volume by using a block of six two-position valves thermostated to 135°C. The end of the reactor was connected directly with this block, which ensured that all the reaction products rested in the gaseous state during the analysis. The threshold sensitivity of the flame ionization detector with respect to maleic anhydride was calculated as $\phi_0 = E/\phi$, where $E_0 = 2E$ of the noise (in mV) and ϕ is the detector sensitivity. The obtained value was $\phi_0 = 0.16 \text{ ng s}^{-1}$ for maleic anhydride.

The reproducibility of preparation was verified for selected catalysts; the absolute selectivity differences did not exceed 2% for individual catalysts.

Parameters. The contact time τ was calculated as $\tau = V_k/r$, where V_k is the catalyst volume (cm³) and r is the flow rate of the mixture (cm³ s⁻¹). The selectivity of formation of maleic anhydride was calculated according to the relation $S_{MA} = 100C_{MA}/(C_{but}^0 - C_{but}^f)$, where C_{MA} is the concentration of maleic anhydride in the reaction mixture and C_{but}^0 and C_{but}^f are the initial and the final (at the outlet) concentrations of butane, all in volume per cent values. The yields of maleic anhydride were calculated as $Y_{MA} = 100C_{MA}/C_{but}^0$, those of carbon monoxide and carbon dioxide as $Y_{CO,CO_2} = 100C_{CO,CO_2}/4C_{but}^0$.

RESULTS AND DISCUSSION

In order to find the optimum V : P ratio, a series of nonmodified catalysts with different vanadium-to-phosphorus ratios was prepared and tested in the reaction of oxidation of butane (1% vol.) with air at 400–520°C. As is evident from Fig. 1, the optimum V : P ratio in the reduced catalyst in the steady state is approximately

1 : 1.2. Similar values have been obtained in the works^{9,10} for contacts prepared by other methods.

Table I (left part) gives the specific rates of oxidation of butane on the catalysts at 470°C, obtained by graphically differentiating the initial segments of the curves of conversion of butane in dependence on the contact time τ . The data fall within the interval of up to 0.2 s, where the dependences are linear and the degree of butane conversion does not exceed 25% (in most cases is below 12%).

TABLE I

Activity and selectivity of V-P-O-M catalysts (V : P = 1 : 1.2)

| Catalyst | M | M : V | S_m^a | W_m^a | t_{optim}^a °C | τ_{optim} s | C^a % | S_{MA}^a % | Y_{MA}^a % | Y_{CO}^a % | Y_{CO_2} % |
|----------|----|----------|---------|---------|----------------------------|----------------------------|------------|-----------------|-----------------|-----------------|-----------------|
| 1 | — | — | 2.4 | 0.13 | 495 | 4 | 80.0 | 39.0 | 31.2 | 35.2 | 14.3 |
| 2 | Pd | 0.2 : 1 | 2.0 | 0.71 | 470 | 6 | 78.3 | 34.8 | 27.2 | 0.0 | 49.6 |
| 3 | Zn | 0.2 : 1 | 2.1 | 0.32 | 470 | 3 | 82.0 | 49.7 | 40.8 | 31.5 | 9.2 |
| 3-1 | Zn | 0.08 : 1 | 1.8 | 0.30 | 520 | 5 | 80 | 47.5 | 38.0 | 30.2 | 12.5 |
| 4 | Cu | 0.2 : 1 | 5.6 | 0.26 | 420 | 4 | 93.0 | 52.8 | 49.1 | 23.4 | 17.0 |
| 5 | Fe | 0.2 : 1 | 3.7 | 0.25 | 420 | 4 | 87.2 | 57.0 | 49.7 | 22.3 | 16.1 |
| 6 | Ni | 0.2 : 1 | 3.2 | 0.20 | 470 | 3 | 87.6 | 35.8 | 31.4 | 36.8 | 17.1 |
| 7 | Cd | 0.2 : 1 | 2.1 | 0.15 | 470 | 4 | 91.9 | 45.8 | 42.1 | 27.7 | 19.8 |
| 8 | Sn | 0.2 : 1 | 2.7 | 0.14 | 470 | 6 | 85.1 | 17.0 | 14.5 | 50.8 | 15.1 |
| 8-1 | Sn | 0.1 : 1 | 5.4 | 0.08 | 470 | 3 | 95.6 | 60.9 | 58.2 | 28.2 | 8.7 |
| 8-2 | Sn | 0.05 : 1 | 3.4 | 0.08 | 470 | 4 | 83.8 | 55.5 | 46.5 | 25.4 | 7.9 |
| 9 | Co | 0.2 : 1 | 2.9 | 0.11 | 470 | 5 | 91.8 | 62.0 | 56.9 | 27.6 | 7.6 |
| 9-1 | Co | 0.5 : 1 | 2.4 | 0.39 | 440 | 3 | 92.9 | 6.0 | 5.6 | 13.6 | 72.5 |
| 9-2 | Co | 0.3 : 1 | 2.3 | 0.23 | 470 | 5 | 94.0 | 33.4 | 31.4 | 29.4 | 30.5 |
| 9-3 | Co | 0.1 : 1 | 3.0 | 0.10 | 470 | 5 | 90.5 | 54.2 | 49.1 | 31.9 | 8.2 |
| 9-4 | Co | 0.05 : 1 | 2.6 | 0.10 | 470 | 5 | 89.5 | 54.4 | 48.7 | 32.7 | 8.4 |
| 10 | Ba | 0.2 : 1 | 2.8 | 0.10 | 520 | 3 | 77.7 | 38.1 | 29.6 | 32.1 | 13.2 |
| 11 | Ce | 0.2 : 1 | 11.2 | 0.10 | 420 | 3 | 88.7 | 47.4 | 42.0 | 33.4 | 14.2 |
| 11-1 | Ce | 0.1 : 1 | 10.5 | 0.09 | 495 | 4 | 90.9 | 46.2 | 42.0 | 35.1 | 12.4 |
| 12 | Mn | 0.2 : 1 | 4.1 | 0.09 | 420 | 6 | 85.2 | 65.4 | 55.7 | 16.0 | 12.4 |
| 12-1 | Mn | 0.5 : 1 | 2.8 | 0.22 | 420 | 3 | 84.8 | 12.0 | 10.2 | 42.5 | 30.3 |
| 13 | Li | 0.2 : 1 | 2.8 | 0.09 | 495 | 6 | 85.9 | 48.0 | 41.2 | 34.1 | 8.2 |
| 13-1 | Li | 0.5 : 1 | 2.5 | 0.09 | 495 | 6 | 86.2 | 49.0 | 42.2 | 31.0 | 10.3 |
| 13-2 | Li | 0.1 : 1 | 2.3 | 0.08 | 495 | 6 | 78.6 | 51.8 | 40.7 | 29.5 | 6.9 |
| 13-3 | Li | 0.05 : 1 | 1.6 | 0.09 | 520 | 12 | 84.9 | 47.7 | 40.5 | 34.4 | 7.6 |

^a S_m specific surface area, $m^2 g^{-1}$; W_m specific rate at 470°C and 1% concentration of butane in air, $\mu\text{mol s}^{-1} m^{-2}$; τ_{optim} optimum contact time; C degree of conversion of butane, S selectivity, Y yield of the substance indicated.

The reaction products in these conditions, in addition to traces of maleic anhydride, hydrocarbons (ethylene, propylene), aldehydes (acetaldehyde, acrolein), and acids (acetic and acrylic acids), are carbon monoxide, carbon dioxide, and water. As the data evidence, additions of Pd, Zn, Cu, Fe, Ni, Cd, and Sn in atomic ratios to vanadium of 0.2 : 1 raise the specific activity of the V-P-O catalyst, whereas those of Co, Ba, Ce, Mn, and Li reduce it to an extent. Moreover, the activity increases further with increasing contents of Co, Sn, and Mn, whereas in the case of Li its concentration in the catalyst does not affect the activity of the contact over a wide region.

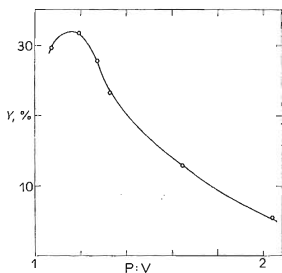


FIG. 1

Dependence of the conversion of butane on the P : V atomic ratio; $T = 470^\circ\text{C}$, $\tau = 3.16$ s, 1% vol. butane in air

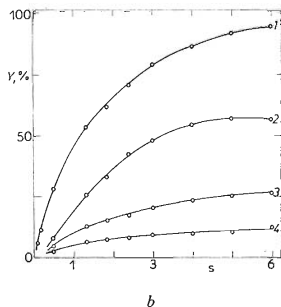
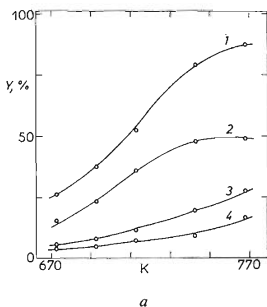


FIG. 2

Dependence of oxidation of butane *a* on τ (at $t = 470^\circ\text{C}$) and *b* on t (at $\tau = 3$ s) for V-P-O-Co catalyst (Co : V = 0.2 : 1). 1 Degree of conversion of butane, 2 yield of maleic anhydride, 3 yield of CO/4, 4 yield of CO₂/4

The temperature dependence of oxidation of butane was also examined in the region of 400–520°C for various contact times. The optimum temperatures and contact periods, for which the yields of maleic anhydride were highest, are given in Table I. As an example, Fig. 2 shows the results obtained on the V-P-O-Co catalyst (Co : V = 0.2 : 1); the dependences for the other catalysts are alike. Typically, in the temperature and time dependences there are points of maximum concentration of maleic anhydride, while the degree of conversion of butane and the concentrations of carbon monoxide and carbon dioxide increase monotonically. Obviously, near the temperatures and contact times where the maleic anhydride concentration is maximum, a consecutive conversion of the anhydride formed starts to play a role.

The data of the specific rate of oxidation of butane give overall information on the activity of the contacts with respect to hydrocarbons, but they are insufficient for characterizing the ability of the catalyst to route the oxidation towards formation of maleic anhydride. This ability can be evaluated as the selectivity of formation of the product in question. The optimum integral selectivities of formation of maleic anhydride, as given in the right part of Table I, lead to the sequence of catalysts (with the modifier-to-vanadium atomic ratio 0.2 : 1) as follows: V-P-O-Mn > V-P-O-Co > V-P-O-Fe > V-P-O-Cu > V-P-O-Zn \approx V-P-O-Li \approx V-P-O-Ce > V-P-O-Cd > V-P-O \approx V-P-O-Ba > V-P-O-Ni \approx V-P-O-Pd > V-P-O-Sn.

This sequence shows that at the same concentration, M : V = 0.2 : 1 (usual in patent data), the selectivity of the parent catalyst is improved by most of the elements, reduced by only three of them, *viz.* nickel, palladium, and tin, and left unaffected by barium. On the other hand, the positions of the catalysts in the series of optimum selectivity with respect to maleic anhydride should not be looked upon as final, as the order does not reflect the effect of the element concentration on the properties of the V-P-O catalyst, on its phase composition and structure. Detailed data concerning the structure and phase composition of the catalysts will be published in a forthcoming paper. Here it should only be mentioned that the data for all the catalysts except those modified by Li, Pd, Cd, or Ba show that a phase of vanadyl diphosphate, $(VO)_2P_2O_7$, is present in them. The results indicate that the additives and this phase form a solid solution. In the palladium-modified catalyst the presence of palladium metal was observed in addition to the vanadyl diphosphate phase, and in the barium-containing catalyst the compound $VO(PO_3)_2$ was found to form to an extent. In the lithium- (Li : V = 0.1 : 1) or cadmium-modified catalyst, an admixture of a compound which seems to be phosphate was found in addition to vanadyl diphosphate. Omitting those catalysts that in addition to $(VO)_2P_2O_7$ contain another phase whose catalytic properties are unknown, and taking into account the effect of concentration of the added element on the catalytic properties of the V-P-O catalysts, we can write the sequence of catalysts with respect to the selectivity of formation of maleic anhydride as follows: V-P-O-Mn (0.2) > V-P-O-Co(0.2) \approx

$\approx V-P-O-Sn(0.1) > V-P-O-Fe(0.2) > V-P-O-Cu(0.2) > V-P-O-Li(0.1) >$
 $> V-P-O-Zn(0.2) > V-P-O-Ce(0.2) > V-P-O > V-P-O-Ni(0.2)$ (the element-to-vanadium atomic ratios are given in parentheses).

This series is interesting from the following point of view. The first five catalysts, with the highest selectivity for maleic anhydride and giving this compound in the highest yields, contain Mn, Co, Sn, Fe, and Cu, hence elements in the ions of which the electron shell is incomplete (the O shell in the case of Sn^{2+} and the M shell in the remaining cases). The three following catalysts, with mutually close selectivities and yields of maleic anhydride, involve Li, Zn, and Ce, whose ions possess complete electron shells (Ce^{3+} is considered in the case of cerium); the yields of maleic anhydride are lower than in the preceding cases.

The series should not be looked upon as final and absolute, as the concentrations of some elements (Fe, Cu, Ni) have not been optimized; in fact, catalysts containing Fe or Cu in a concentration better approaching the optimum value might possibly occupy a higher place in the series. Still, it can be concluded that a relatively high selectivity and high yields of maleic anhydride are attained on catalysts containing elements, the ions of which possess incomplete electron shells. The catalyst containing nickel, whose ions also possess an incomplete electron shell, is an exception: the experimental selectivity for maleic anhydride is considerably poorer than as would be expected. Probably, nickel — similarly as palladium — does not form a solid solution with $(VO_2)_2P_2O_7$, but separates as an X-ray-amorphous phase (palladium separates as a crystalline metallic phase).

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