OXIDATION OF BUTANE TO MALEIC ANHYDRIDE ON UNMODIFIED AND MODIFIED VANADIUM-PHOSPHORUS CATALYSTS*

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Properties of modified vanadium-phosphorus catalysts were studied and compared with the unmodified catalyst in the oxidation of butane. The highest promoting effect has been achieved by introducing cobalt to the catalyst lattice. At 90% conversion, the yield of maleic anhydride amounted to 59 mole per cent. The catalyst modified by cobalt increased the specific rate of butane oxidation and maleic anhydride formation three times compared to the unmodified catalyst. The specific activity of the catalysts decreased in the following order: $Co > U \approx Ce > V\text{-}P\text{-}O > K \approx Mo$.

One of the most perspective applications of the catalysts based on phosphorus and vanadium oxides is their use for selective oxidation of the C_4 fraction, the final product of which is maleic anhydride (further MA).

It is generally accepted that vanadium-phosphorus catalysts are complex system[1–7], in which the most efficient and selective appears to be the $(VO)_2P_2O_7$ phase[8]. This phase is also an efficient component of industrial catalysts for partial oxidation of even the less reactive butane to MA. Other phases present are e.g. crystalline forms of $VOPO_4$, undesired condensed phosphates such as $VO(PO_3)_2$ or $V(PO_3)_3$. The IR spectra indicate[6,7] also the presence of $(VO)_2P_4O_{12}$. Discussion about what phases exist in the stabilized catalysts still continues, despite of the agreement of majority of authors on the $(VO)_2P_2O_7$ phase with V(IV) oxidation state as prevailing.

It was shown that the method of preparation of catalyst precursor, its treatment and finally also the way of its activation affect the resultant properties of the stabilized catalyst[6,9,10]. All these processes determine the oxidation state of vanadium, deviations in phase composition, in the structure and in lattice defects, the state of catalyst surface, etc. (refs[11–13]).

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The effective means of improvement of catalytic properties of these catalysts is the introduction of metal modifiers to their lattice[14]. In spite of a number of studies dealing with the use of unmodified catalysts in the title reaction, only a few works have been concerned with the application of modified ones, and that mostly in the patent literature[11].

Probably the first original work which systematically dealt with the effect of various modifiers on improvement of catalyst properties was that by Brutovsky et al.[14]. Hodnett[2] and Hutchings[11] surveyed reported data on these catalysts, the latter author making an attempt at elucidating the role of a given modifier. The data reported at that time led the author to assume that the predominant role of the modifier is to affect the structure characteristics of catalyst phases. The question about the mechanism by which these modifiers improve catalytic properties has till now remained unanswered. As to the cation of modifier (further M) incorporated into V-P catalyst, Hutchings sees its role also in its effect on adsorption of oxygen and its diffusion within the lattice, by which a nonselective route of butane oxidation is supressed.

Of the latest works concerned not only with general aspects of the reaction on modified V-P-M-O catalysts but also with the effect of modifiers on the structure and morphology of the catalysts in optimizing selective butane oxidation to MA, the following ones deserve citation[15–19].

The aim of the present work was to prepare a series of unmodified and modified vanadium-phosphorus catalysts, using the same procedure for their synthesis and activation, and to compare their catalytic properties.

EXPERIMENTAL

Synthesis of Catalysts

The procedure reported earlier[20] was used to prepare all catalyst precursors. The V-P-O precursor was obtained by dissolving V_2O_5 in refluxing concentrated hydrochloric acid. Then, to the cooled solution, H_3PO_4 was added in the amount ensuring the V : P molar ratio = 1.2, and the mixture was again maintained under reflux. After solvent evaporation, the solid was dried in air at elevated temperature, then it was crushed and sieved to obtain the required grain size. When preparing the modified catalyst with the M : V molar ratio = 0.14, the modifier was added to the solution before reaction with H_3PO_4 as the chloride or in the case of Co as the acetate.

All the precursors were first subjected in a glass reactor to fast heating to 470 °C in a stream of nitrogen, followed by immediate cooling to 450 °C. Then the activation was made by the reaction mixture, which involved 1.3 to 1.5 vol.% of butane in air. The activation process[12] was effected by using different flow rates and lasted until 90 to 92% butane conversion has been achieved. The methods of chemical analysis of the catalysts were reported briefly elsewhere[6,13,20].

Determination of Specific Surface Area

The surface of individual catalysts after the reaction was determined chromatographically, using thermal desorption of argon (the starting mixture contained 13 vol.% of argon in helium). The desorption peak of argon was evaluated, and the specific surface area was obtained with the use of the standards, the surface of which was known and determined by BET method (Al_2O_3 or TiO_2).

Catalytic Measurements and Analysis of Reaction Products

Catalytic properties of individual V-P catalysts were determined in an integral flow, fixed-bed reactor. The catalyst (4 cm^3) of 0.63 – 0.80 mm grain size was activated in the reaction mixture containing 1.3 – 1.5 vol.% of butane in air. After catalyst stabilization, the measurements were carried out at 450 °C and with varying contact times τ (from 0.3 to 6.0 s). The temperature along the catalyst bed was uniform, which was ensured by the reactor construction[21].

Reaction products were analyzed on two Chrom 4 chromatographs, one of which was equipped with a flame ionization detector and the other with a thermal conductivity detector. Quantitative analysis of the entering reaction mixture as well as of the products was made essentially by two procedures: (i) by evaluation of chromatographic signals with the use of the connected computer unit (Data Monitor II, Watrex Prague) working with a special programme, and (ii) by the usual way, i.e. by weighing chromatographic peaks corresponding to individual components, using calibration graphs.

Further details on determination of catalytic properties are given elsewhere[12]. Most experiments were at least twice repeated.

RESULTS AND DISCUSSION

In the present work we have studied catalytic properties of unmodified and modified vanadium-phosphorus catalysts which have incorporated one of the following metal elements: Co, Ce, U, Mo, and K. All the catalysts had the same composition (P : V molar ratio = 1.2 and the modifier to vanadium molar ratio (M : V) = 0.14), which was close to the optimum one[14,22]. Experiments were carried out for different contact times τ (from 0.3 to 6.0 s) at 450 °C.

Experimental results are represented graphically in Fig. 1. For mutual comparison of individual catalysts modified with metal ions as well as with the unmodified V-P-O catalyst, the effect of the contact time τ on butane conversion (X, mole %, curve *1*) and the yield of MA (Y_{MA}, mole %, curve *2*) was followed. From these two dependences, the curve of selectivity (S) of MA formation (curve *3*) was constructed. In all experiments also the dependence of CO and CO_2 yields on τ (curve *4* and *5*, respectively) was recorded.

From the shape of dependence of butane conversion on τ it follows that under identical experimental conditions, the catalysts modified with Mo and K (curve *1*, Figs 1*b* and 1*c*) are less efficient compared to the unmodified V-P-O catalyst (curve *1*, Fig. 1*a*). On the other hand, V-P-Co-O, V-P-Ce-O, and V-P-U-O catalysts (curve *1*, Figs 1*d* – 1*f*) afforded higher butane conversions than the parent V-P-O catalyst over the whole contact time region measured.

The catalysts modified with Co, Ce, and U produce also higher amounts of MA compared to V-P-O catalyst, being mutually comparable in the case of V-P-Co-O (curve *2*, Fig. 1*d*) and V-P-Ce-O (curve *2*, Fig. 1*e*) catalysts. On the other hand, at the same contact time chosen, the nearly same MA yield is obtained with the catalysts

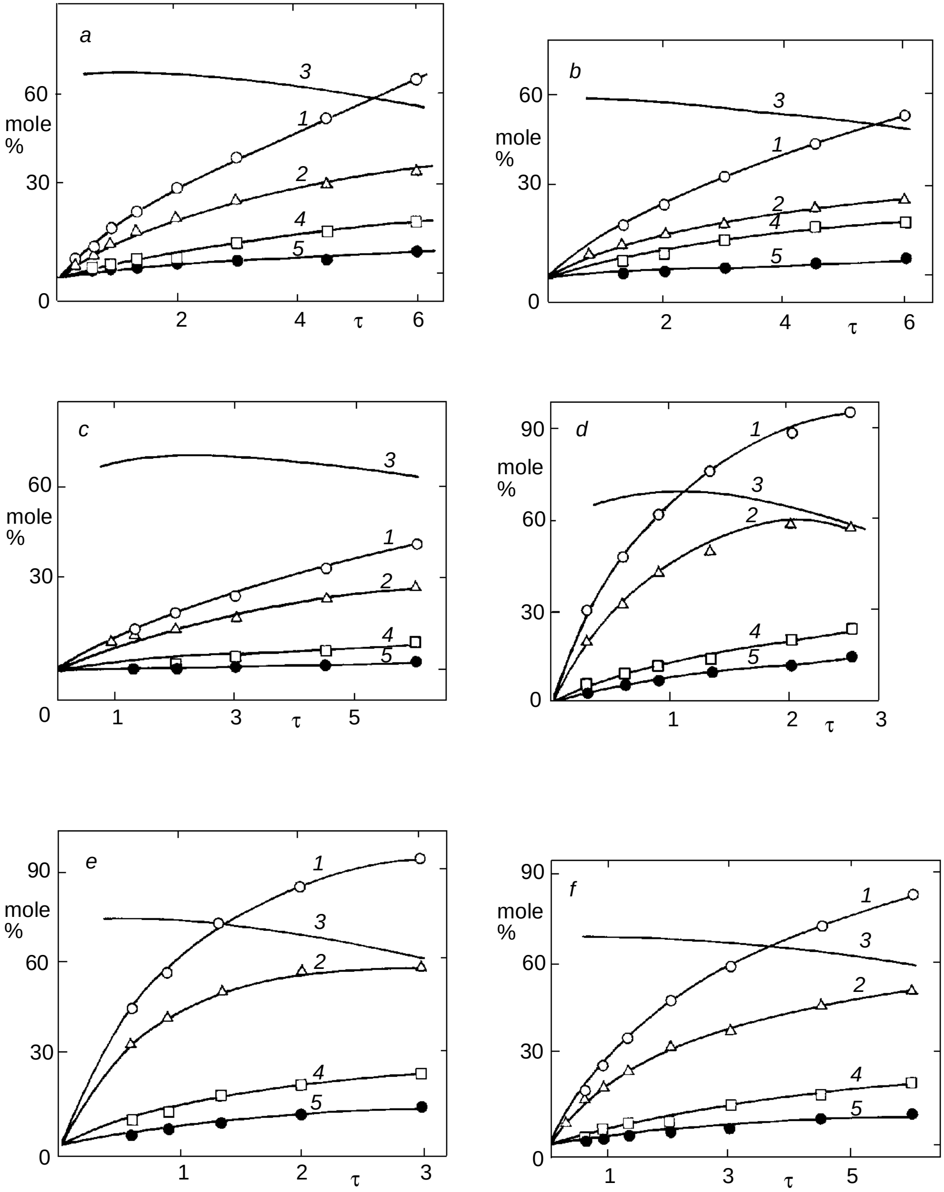

FIG. 1

Dependence of *1* butane conversion (X), *2* MA yield (Y_{MA}), *3* selectivity to MA (S), and yields of *4* CO (Y_{CO}) and *5* CO_2 (Y_{CO_2}) at 450 °C on contact time τ (s). *a* V-P-O catalyst, *b* V-P-Mo-O catalyst, *c* V-P-K-O catalyst, *d* V-P-Co-O catalyst, *e* V-P-Ce-O catalyst, *f* V-P-U-O catalyst modified with K and Mo (curves *2* in Fig. 1*b* and 1*c*, respectively) but always lower with respect to the unmodified catalyst (curve *2*, Fig. 1*a*).

For selectivity determination of MA formation, experimental data from the dependences of butane conversion and MA yield on contact time τ were treated by procedure described earlier[14] for all the catalysts. The dependence of the selectivity on τ at longer contact time tends to decrease, most likely due to a partial oxidation of MA to degradation products. These are the products of total butane oxidation as well as aldehydes, acetic acid, and acrylic acid[16,18].

TABLE I
Basic parameters of catalysts for partial oxidation of butane to MA at 450 °C (for designation of the parameters X, Y_{MA}, and S (see Symbols)

Catalyst	$\tau = 0.3$ s			$\tau = 2$ s		
	Y_{MA}	X	S	Y_{MA}	X	S
V-P-Co-O	19.0	29.0	65.5	59.0	91.5	64.5
V-P-Ce-O	18.9	26.5	71.3	56.5	85.5	66.1
V-P-U-O	7.2	11.6	62.1	31.5	47.5	66.3
V-P-O	4.0	6.0	66.7	19.0	28.5	66.7
V-P-Mo-O	2.7	4.5	60.0	14.2	25.0	56.8
V-P-K-O	2.2	3.5	62.8	14.0	19.9	70.4

TABLE II
Specific rates of butane oxidation r_X (mol s^{-1} m^{-2}) and MA formation r_{MA} (mol s^{-1} m^{-2}) at 15% butane conversion

Catalyst	s^a	τ^b	$Y_{MA}{}^c$	$r_X \cdot 10^8$	$r_{MA} \cdot 10^8$
V-P-Co-O	5.8	0.14	9.8	14.4	9.4
V-P-Ce-O	11.3	0.17	11.6	6.1	4.7
V-P-U-O	2.8	0.50	12.2	7.0	5.6
V-P-O	2.8	0.87	10.6	4.3	3.0
V-P-Mo-O	2.9	1.18	10.8	2.7	2.0
V-P-K-O	2.4	1.48	13.6	2.9	2.6

[a] Specific surface area of the catalyst (m^2 g^{-1}). [b] Contact time (s) at 15% butane conversion. [c] The yield of MA (mole %) at 15% butane conversion.

Table I provides better comparison of the catalytic parameters of investigated catalysts which are arranged here according to the decreasing MA yield. Analysis of the results shows that V-P-Co-O and V-P-Ce-O catalysts give the highest yields of MA with high selectivity and high butane conversion compared to the unmodified V-P-O catalyst. Similarly, also V-P-U-O catalyst shows better catalytic properties than the unmodified catalyst but it does not attain the parameters of both above mentioned catalysts. The results further document that V-P-K-O catalyst is selective but when compared to the other catalysts, the butane conversion achieved is substantially lower. When compared to the catalyst modified with K, V-P-Mo-O catalyst shows comparable MA yields, somewhat higher butane conversion, and the lowest selectivity of MA formation. Hence, these two catalysts are inferior to the catalysts modified with Co, Ce, and U. Also in comparison with the unmodified catalyst, they give worse results.

The results were also used to determine specific rates of butane oxidation and MA formation. In this case, only linear parts of the dependences of butane conversion and MA yield on contact time τ (which correspond to 15% conversions) were treated, using relations described earlier[12].

The results given in Table II prove that the modification of V-P catalyst by metal ion is the important factor influencing its catalytic activity. As the measure of the catalyst activity, one can take both the specific rate of butane oxidation and especially the specific rate of MA formation. The catalyst modified with cobalt is most active, increasing the specific rate of both processes more than three times, compared to the unmodified vanadium-phosphorus catalyst. On the other hand, the activity of the catalysts modified with K and Mo is lower than that of the V-P-O catalyst. These data leads to the following activity order (only the modifier is given):

$$\text{Co} > \text{U} \approx \text{Ce} > \text{V-P-O} > \text{K} \approx \text{Mo} .$$

The unambiguous explanation of the effect of these modifying additives based on their chemical character is at present difficult. It seems likely that their effect relates to the acid-base properties of metal ions built in the catalyst[9,18,22].

SYMBOLS

r_X	specific rate of butane oxidation, mol s^{-1} m^{-2}
r_{MA}	specific rate of MA formation, mol s^{-1} m^{-2}
S	selectivity of maleic anhydride formation, mole %
s	specific surface area, m^2 g^{-1}
X	conversion of butane, mole %
Y_{MA}	yield of maleic anhydride, mole %
Y_{CO}	yield of carbon monoxide, mole %
Y_{CO_2}	yield of carbon dioxide, mole %
τ	contact time, s

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