

VANADIUM-PHOSPHORUS CATALYSTS MODIFIED WITH MAGNESIUM, CALCIUM AND BARIUM

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Vanadium-phosphorus catalysts specially modified with promoters can ensure an efficient and selective oxidation of C₄ hydrocarbons, even also that of butane to maleic anhydride. The catalysts with incorporated Mg, Ca or Ba ions provide a higher conversion of butane, yield of maleic anhydride, and selectivity for the latter compound than the unmodified catalyst. The conversion of butane and yield of maleic anhydride decrease with increasing basicity of the incorporated modifiers in the order: Mg, Ca, Ba, however, the selectivity of formation of maleic anhydride increases in the opposite order, which is interpreted by the idea that on the modified V-P catalysts the conversion of butane decreases faster than the yield of the anhydride with the natural basicity of the above-mentioned modifiers.

Key words: Butane oxidation; Maleic anhydride; Vanadium-phosphorus catalysts; Promoters.

The catalysts based on vanadium and phosphorus oxides have been used in the commercially important selective oxidation of C₄ hydrocarbon fraction to maleic anhydride (MA) since mid 70's already. As their physicochemical and catalytic properties depend on a number of factors, these catalysts continue to be a subject of systematic research.

At present attention has been increasingly focused on the problem of improving their catalytic properties by incorporating some metal ions, the so-called modifiers (M), into their lattice (patents¹⁻⁴). Only recently, also the number of original papers dealing with V-P-M-O catalysts has been increasing⁵⁻⁹. A variety of metals from the periodic system have been used as the modifiers, and published data indicate their influence on the yield and selectivity of formation of MA and on the reaction rate on these catalysts (for reviews, see refs¹⁰⁻¹²). Out of those mentioned only the papers^{7,10} discuss the mechanism of operation of the modifiers. The authors presume that the modifiers perform complex functions in the catalysts: they modify the properties of the (VO)₂P₂O₇ phase, which is generally considered the most important in the polyphase vanadium-phosphorus catalyst¹⁰, they form solid solutions that direct the catalytic activity of the solid phase¹³, and they also affect the rate of the rate-limiting reaction stage – the splitting off of the proton from butane^{7,14}.

In continuation with the previous studies^{9,13,15} also the aim of the present paper is to investigate the effect of some other selected metals, *viz.* Mg, Ca, Ba, on catalytic properties of the correspondingly modified vanadium–phosphorus catalyst and explain the role of modifier.

EXPERIMENTAL

Most experimental conditions were described in previous papers^{9,13}. The unmodified precursor was prepared by refluxing a mixture of V_2O_5 and concentrated HCl. After adding H_3PO_4 in the amount ensuring the final molar ratio of P : V = 1.2 the refluxing was continued. The solvent of the light green-blue suspension obtained was evaporated and the residue was dried at enhanced temperature, ground and sieved to obtain the required grain size.

The precursors of metal-modified catalysts were prepared by adding the respective amounts of the chlorides ($MgCl_2$, $CaCl_2$, $BaCl_2$) – to obtain the required molar ratio of M : V = 0.14 – before the refluxing with H_3PO_4 , the rest of synthesis being identical with that for the unmodified catalyst precursor.

Before the catalytic measurements, both the unmodified and modified precursors were at first formed and then activated by a known procedure⁹. In order to obtain reproducible results, each catalyst was activated until it gradually reached a 90–95% conversion of butane by a choice of contact time at the temperatures of 450–470 °C.

The selective catalytic oxidation of butane (a mixture of 1.1 to 1.4 vol.% of butane with air) to MA was carried out in an integral through-flow reactor. The glass reactor containing the catalyst (4 cm³, grain size 0.6–0.8 mm) was heated in such a way that the temperature of 450 °C along the catalyst bed remain constant¹⁶. The gaseous reaction products passed through the apparatus parts heated above 135 °C to prevent condensation of MA and were analyzed (like the entering reaction mixture) on two gas chromatographs Chrom 4 with a flame-ionization and a heat-conductivity detectors.

The chemical analysis of individual components of catalysts is described briefly elsewhere¹⁷.

RESULTS AND DISCUSSION

In order to determine the effect of the individual cations (Mg, Ca, Ba) incorporated in the lattice of the vanadium–phosphorus catalyst on its catalytic properties, we carried out a series of experiments estimating the dependence of conversion of butane, yields of MA, CO and CO₂ on the contact time τ (*i.e.* the ratio of catalyst volume in cm³ to the volume flow rate in cm³ s⁻¹). The catalysts compared had the molar ratios of P : V = 1.2 (*i.e.* slight excess of phosphorus) and M : V = 0.14. In general, the optimum amounts can differ for individual modifiers, but according to our experience the above-given value is close to the optimum amount of most metal additives¹⁸. The measurements were realized at the contact times of 0.3–0.6 s at the working temperature of 450 °C.

The catalytic properties are known to be influenced by the method of preparing and way of forming and activating even in the case of the unmodified catalyst^{19,20}, which is explained by partial changes in kind and proportion of phases^{21,22}, proportion of crystalline and amorphous phases^{20,22}, lattice defects^{15,19,22} as well as acid-base properties of the surface^{7,23}. Various ways of preparation result in different characteristics of volume

and – first of all – surface characteristics of the catalyst. By the incorporation of modifiers into the catalyst lattice this variability is still increased, depending on chemical nature of the additive. The changes in physical and chemical characteristics of catalyst volume and surface must be reflected in the catalytic properties of the modified vanadium–phosphorus catalysts. This is interpreted by the effect of chemical nature and concentration of modifier on the number and strength of the Lewis or Brønsted acidic sites which affect the course of the rate-limiting step, *i.e.* splitting off of the proton from butane molecule, and by the fact that the necessary Brønsted acidic sites facilitate the desorption of MA (which is also acidic in nature). The important factors affecting the change of catalytic properties also include the effect of modifiers on the lattice defectiveness^{15,19,22}.

The experimental results obtained are graphically presented in Figs 1a–1d. It can be seen that the increase in both butane conversion and MA yield with increasing contact time is higher with the modified catalysts than with the unmodified one in the whole range measured. Furthermore it can be stated that at all the contact times these parameters are highest for the magnesium-modified catalyst (Fig. 1b), being lower for the calcium modified one (Fig. 1c) and lowest in this series for the barium-modified one (Fig. 1d). The selectivity of MA formation (curve 3, Figs 1b–1d) is higher when compared with that for the unmodified catalyst (Fig. 1a), but the differences between the individual modified catalysts are small at short contact times.

Table I gives concrete catalytic data for selected contact times. Obviously, the modifiers used increase the butane conversion, MA yield, and selectivity of MA formation as compared with the unmodified catalyst. The basic catalytic data presented, except for the selectivity, decrease with increasing natural basicity of the metal modifier. From the results in Table I it also follows that the differences in selectivity between the individual modified catalysts increase with increasing contact times. We can see a trend of increasing selectivity of MA formation when going from magnesium to barium,

TABLE I

Butane conversion values (*X*), MA yields (*Y*), and MA formation selectivities (*S*), in mole %, for selected contact times (τ) at 450 °C

Catalyst	0.3 s			2.0 s			6.0 s		
	<i>X</i>	<i>Y</i>	<i>S</i>	<i>X</i>	<i>Y</i>	<i>S</i>	<i>X</i>	<i>Y</i>	<i>S</i>
V–P–O	6.2	3.9	62.9	29.3	18.5	63.1	64.7	34.7	53.6
V–P–Mg–O	13.0	9.0	69.2	53.0	35.5	67.0	93.0	54.5	58.6
V–P–Ca–O	11.3	7.7	68.1	48.3	33.5	69.4	83.0	51.0	61.4
V–P–Ba–O	6.8	4.8	70.6	29.3	20.5	70.6	54.0	37.0	68.5

which agrees with increasing natural basicity of the added modifier. Although it is generally supposed that an increase in number or strength of basic centres at the surface of vanadium–phosphorus catalysts results in a firmer bonding of acidic products (hence also MA) at the catalyst surface during the selective oxidation of butane, no corresponding selectivity decrease was observed which would indicate possible additional oxidation (giving the product of total oxidation) of acidic intermediates or MA during their prolonged presence at the catalyst surface. In our opinion, the effect of the acid–base relations at the catalyst surface on the course of the reaction in question is more complex. The results given in this paper as well as other experimental results obtained

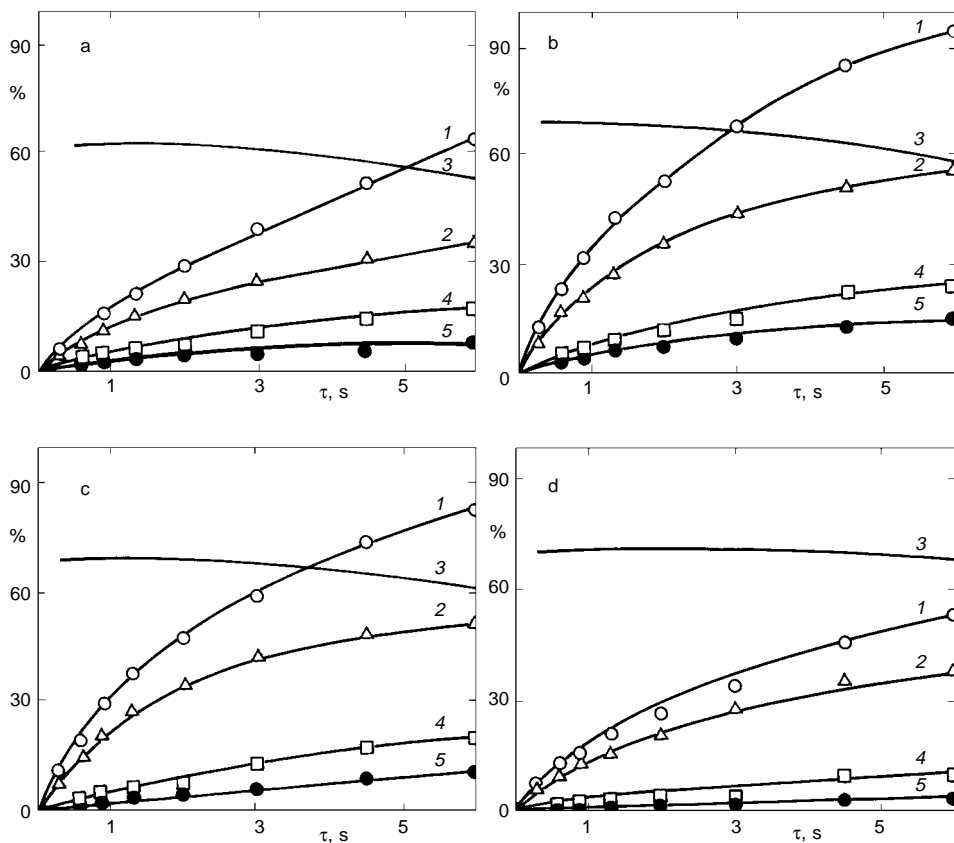


FIG. 1

Dependence of butane conversion (1), MA yield (2), MA formation selectivity (3), and CO and CO₂ yields (expressed by the butane consumed) (4 and 5, respectively) on contact time in partial oxidation of butane at 450 °C. a V–P–O catalyst, b V–P–Mg–O catalyst, c V–P–Ca–O catalyst, d V–P–Ba–O catalyst

by us with modified catalysts indicate that the acid–base relations at the surface show an optimum with regard to the course of selective oxidation. This fact shows that a deeper study of the influence of modifiers, structural characteristics of the catalyst, phase composition and other factors on the number and strength of the Lewis and Brønsted centres and their proportions will be necessary.

From the experimental results given it follows that, in accordance with the increase of natural basicity from magnesium to barium, the butane conversion decreases faster than the MA yield, which partially increases the catalyst selectivity.

The catalytic activity is more realistic characteristics of a catalyst than its basic catalytic properties. Preliminarily it can be stated that the specific surface of the unmodified catalyst prepared in the medium of hydrochloric acid is lower than $3.0 \text{ m}^2 \text{ g}^{-1}$, whereas that of the modified catalysts lies in the interval of $4.0\text{--}5.5 \text{ m}^2 \text{ g}^{-1}$. Thus it can be stated that the initial specific rate (expressed in $\text{mol s}^{-1} \text{ m}^{-2}$) of butane oxidation will be higher for the modified catalysts (except for that containing barium) than for the unmodified catalyst. The same is also true for the specific rate of formation of MA.

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