

## **Effect of Additives to VPO System on Its Catalytic Properties in Oxidative Dehydrogenation of Propane and Ethane**

by **M. Gašior<sup>1</sup>**, **I. Gressel<sup>1</sup>**, **V.A. Zazhigalov<sup>2</sup>** and **B. Grzybowska<sup>1</sup>**

<sup>1</sup>*Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,  
ul. Niezapominajek 8, 30-239 Kraków, Poland*

<sup>2</sup>*Ukrainian-Polish Laboratory of Catalysis, Institute of Sorption and Problems of Endoecology,  
NASU, ul. Gen. Naumova 13, Kyiv-164, 03164, Ukraine*

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Oxidative dehydrogenation (ODH) of propane and ethane has been studied on VPO catalysts with additives of Bi, La, Mo and Zr. The catalysts show promising properties in the ethane ODH, with selectivities to ethene of ~85% at 10% conversion of ethane, but are poor in the propane ODH (maximal selectivities to propene of ~40%). For both alkanes introduction of the additives leads to an increase in the overall rate of the reaction. The effect of the additives on the selectivity to olefins is complex and depends on the reaction temperature, the additive content and the type of alkane. The same additive has in several cases an inverse effect on the selectivity for the propane and ethane ODH. The Mo additive and higher amounts of the La additive increase the selectivity to propene, whereas they decrease the selectivity to ethene. Low content of La additive gives rise to the increase of selectivity to ethene and decrease in that to propene. The differences between the selectivities to olefins in ODH of propane and ethane are discussed as being due to different acido-basic properties of the propene and ethene and their different strength of bonding to the catalyst surface.

**Key words:** VPO catalysts, propane, ethane: oxidative dehydrogenation

Lower alkanes have been considered in the last years as cheap raw materials for petrochemical catalytic processes, in particular for production of olefins and oxygenated compounds, such as aldehydes, organic acids and anhydrides [1–5]. The only industrial process based on alkanes, realized so far, is the oxidation of n-butane to maleic anhydride on oxide V-P-O catalysts [4,6–8].

In the last years oxidative dehydrogenation, ODH of alkanes has attracted much interest as a source of olefins for polymerization or for their further oxidation to oxygen-containing products [1–3,5]. The ODH reactions are more advantageous in comparison with classical dehydrogenation, DH, used at present on the industrial scale to obtain olefins. Their exothermicity, high values of equilibrium constants and the absence of coke permit to conduct the reaction at relatively low temperatures with higher yields, and to avoid troublesome regeneration of catalysts, required in DH reactions to remove the coke. The disadvantage of the ODH reactions is, on the other hand, the formation of carbon oxides by parallel to ODH total oxidation of alkanes or consecutive oxidation of the olefins formed. This is the main reason that, in spite of numerous studies, no large-scale process based on ODH of lower alkanes has been

proposed yet. The research is then still conducted aiming at selection of efficient catalysts for these reactions and at elucidation of their mechanism.

Among the transition oxides systems, those containing vanadium as vanadia dispersed on oxide supports, *e.g.* TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> [9–12], or in definite compounds, such as magnesium vanadates [13–15], have been found promising for ODH of lower alkanes, in particular of propane, with the propene yields of 10–15% and selectivities at ~10% conversion of ~60–70%. The V-P-O system has been found active, though not selective, in the ODH of propane and ethane [16,17]. Recent data have shown, however, that the introduction of the Bi additive to the V-P-O catalysts improves the yield of the olefin in the ODH of ethane [18]. The effect of the Bi additive has been ascribed to the favourable modification of the structure and electronic properties of the active V-O-V centre in vanadyl pyrophosphate by the incorporation of an atom of big atomic radius such as Bi, rendering the oxygen atom in the centre more basic.

It seemed then of interest to check the effect of the additives of Bi and other ions of big atomic radius to these catalysts on the catalytic performance in the ODH of another alkane, *i.e.* propane and to compare it with the data of ethane.

In the present work the V-P-O catalysts containing the additives of Bi, La, and Zr ions have been then tested in ODH of propane and ethane.

## EXPERIMENTAL

**Preparation of the catalysts:** The V-P-O catalysts were obtained from the mixture of vanadia, o-phosphoric acid (the P/V ratio 1.15) and precursors of the additives (nitrates of Bi and La and ZrOCl<sub>2</sub>) in an n-butanol medium with a method described in [19]. The method consisted in heating of the mixture with continuous stirring at 110°C for 16 h, evaporation of n-butanol in vacuum for 40 h and heating at 270–300°C. The catalysts were activated at 500°C in the reaction mixture. Table 1 gives the list of the samples, their specific surface area, determined with the BET method. XRD technique has shown, that after the activation the samples contained (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> as a main phase.

**Table 1.** List of samples in V-P-O system with additives and total rate of propane and ethane reaction with oxygen at 400°C.

Catalyst symbol	Ad/V	S <sub>sp</sub> [m <sup>2</sup> /g]	V <sub>400</sub> 10 <sup>5</sup> mol m <sup>-2</sup> min <sup>-1</sup>	
			C <sub>3</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>6</sub>
VP	0	11.0	0.06	0.07
VPBi 0.2	0.2	14.0	0.07	0.06
VPBi 0.3	0.3	16.0	0.14	0.15
VPLa 0.1	0.1	16.9	0.13	0.07
VPLa 0.4	0.4	19.6	0.17	0.07
VPZr 0.2	0.2	19.2	0.10	0.10
VPZr 0.4	0.4	20.4	0.15	0.17
VPMo 0.3	0.3	10.6	0.14	< 0.05

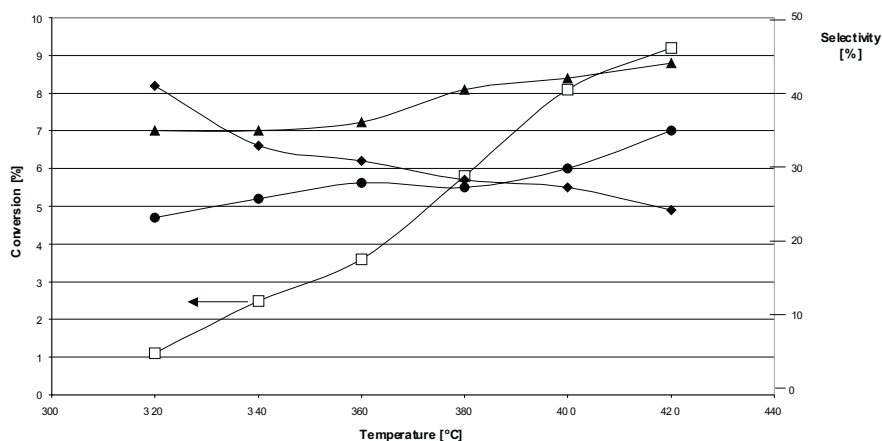
**Catalytic test.** Catalytic activity of the samples in oxidative dehydrogenation of propane and ethane was measured in a fixed bed flow apparatus between 320–420°C (propane ODH) and at 400 and 450°C (ethane ODH). The reactor (13 mm in diameter) was made of stainless steel, the thermocouple being placed coaxially in the catalyst bed. Analysis of products and unreacted alkanes was performed by on-line gas chromatography, using Hewlett-Packard chromatograph with catharometric detection. The composition of the reaction mixtures was: alkane:oxygen:helium = 7:3:90 (in vol%), the constant flow of the reactants being maintained by mass flow controllers. Since the selectivity in the ODH reactions is usually compared at the same value of total conversion (the reaction has a consecutive character), to obtain the comparable conversions (of ~10%) the contact time was varied for different samples and different alkanes between 0.5 and 2 s. The variation of the contact time was realized by changing the total flow rate of the reaction mixture and the amount of a sample (0.5 or 1 ml). C<sub>3</sub>H<sub>6</sub> (in propane ODH), C<sub>2</sub>H<sub>4</sub> (in ethane ODH), CO and CO<sub>2</sub> were found as main reaction products, the amount of oxygenates was below 1% of the total amounts of products. The samples were kept at a given temperature till a constant value of the alkane conversion and the yields of products were obtained (usually after 2–3 h). The selectivities to different products were calculated from the formula:  $S_i = c_i / \sum c_i$ , where  $c_i$  are concentrations of products  $i$ . The total conversion values  $X_p$  were calculated as:

$$X_p = \frac{c_p^0 - c_p}{c_p^0}$$

where  $c_p^0$  and  $c_p$  are the concentrations of propane or ethane at the inlet and outlet of the reactor, respectively.

## RESULTS AND DISCUSSION

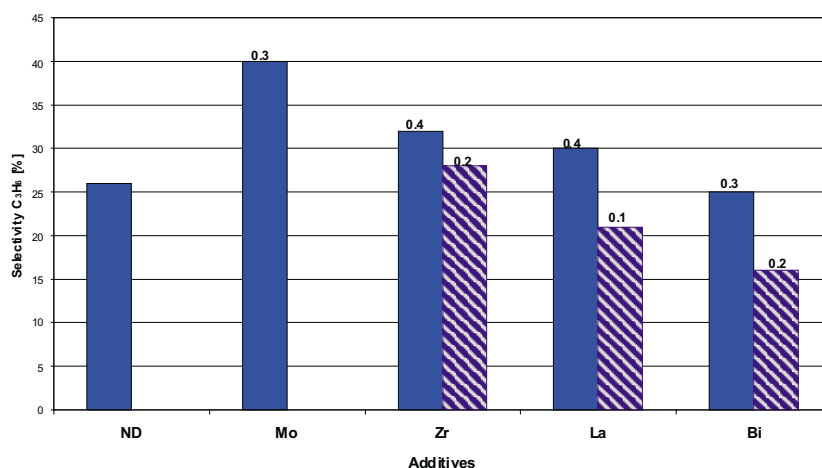
Fig. 1 presents changes of the propane conversion and selectivities to propene, CO<sub>2</sub> and CO with the reaction temperature for VP Bi 0.3 catalyst. The increase of the conversion with the temperature is accompanied by the decrease in the selectivity to propene and increase in the selectivity to CO and CO<sub>2</sub>. This behaviour, typical for the ODH reactions of lower alkanes on oxide catalysts [1–3, 11, 12], has been also observed for other catalysts of the studied VPO series with the additives, both for the pro-



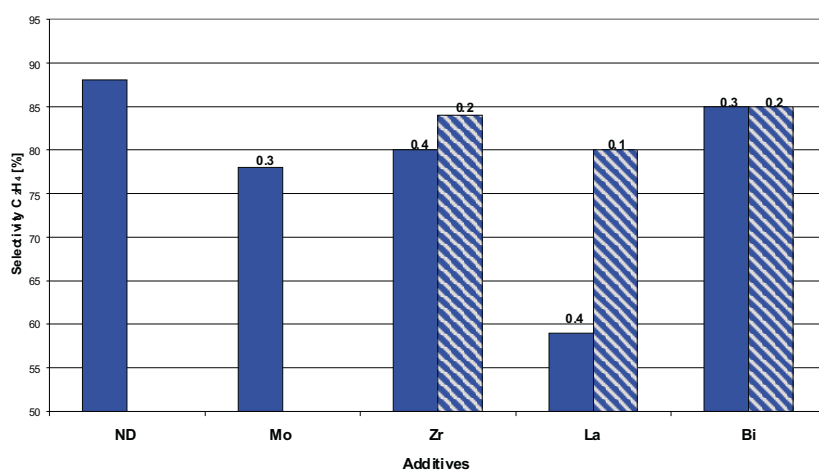
**Figure 1.** Changes of conversion (□) and selectivities to C<sub>3</sub>H<sub>6</sub> (◆), CO (▲) and CO<sub>2</sub> (●) with the reaction temperature for oxidative dehydrogenation of propane on VPBi 0.3 catalyst.

pane and ethane ODH. In the further studies the catalysts were compared for the reaction temperature of 400°C.

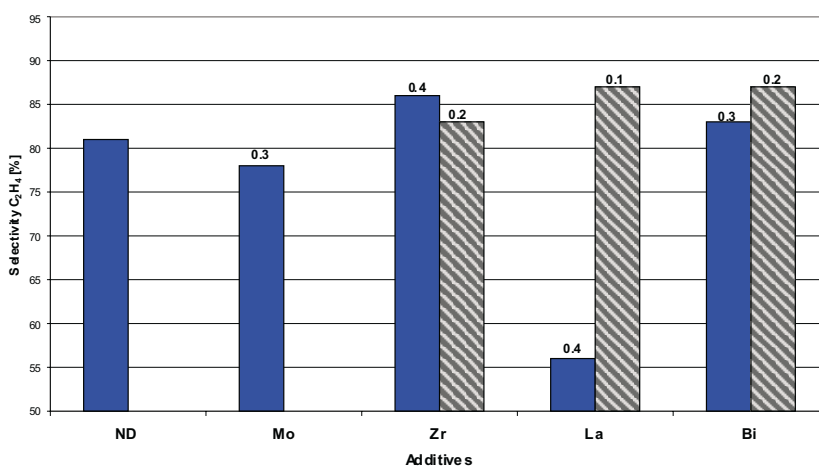
The total rates of the propane and ethane reactions at this temperature,  $V_{400}$  are given in columns 4 and 5 of Table 1. As seen, the introduction of the Bi, La, Zr, and Mo additives into the VPO system leads generally to the increase in the reaction rate for both the ODH reactions, this increase being more evident for the higher additive content. The selectivities to olefins at 400°C and at the alkane total conversion of 8–10% for the studied catalysts are given in Fig. 2 (propene from ODH of propane at 400°C) and Fig. 3 and 4 (ethene from ODH of ethane at 400 and 450°C, respectively).



**Figure 2.** Selectivity to propene [at ~10% conversion] for VPO catalysts with the additives. Reaction temperature 400°C, ND – VPO catalyst without additives.



**Figure 3.** Selectivity to ethene [at ~10% conversion] for VPO catalysts with the additives. Reaction temperature 400°C, ND – VPO catalyst without additives.



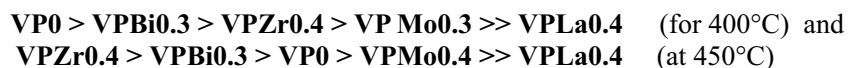
**Figure 4.** Selectivity to ethene [at ~10% conversion] for VPO catalysts with the additives. Reaction temperature 450°C, ND – VPO catalyst without additives.

The effect of the additives on the selectivity depends on the nature of the additive and its content, and is different for the propane and ethane reactions. For the higher additive content the selectivities to propene at comparable propane conversions (8–10%) are higher (with the exception of VPBi sample) than the selectivity for the non-promoted catalyst VPO, decreasing in the sequence (Fig. 3):



Higher selectivities to the desirable product with the higher total reaction rate for the promoted samples indicate higher yields of propene. Still, it should be observed that the highest selectivity, observed for the VPMo catalyst (40% at 10% conversion) and the propene yield (~4%) are considerably lower than those reported for the best systems in the ODH of propane (VMgO and CoNi-molybdate). It appears then that even after the modification with the additives, the VPO-based catalysts are not promising for the ODH reaction of this alkane. For the lower additive content the selectivities are lower as compared with that of the non-promoted sample (with the exception of the VPZrO catalyst).

The ethene selectivities at 400°C for the higher additive contents decrease in the sequence:



The effect of the additives on the selectivity is then rather complex, depending on the nature of the additive and on the reaction temperature. In view of the higher reaction rates for the samples with the additives as compared with undoped VPO catalyst introduction of the additives should lead, however, to higher ethene yields confirming the favourable effect of the additives to VPO system on the ODH of ethane reported earlier for the Bi additive [18].

On the other hand, the ethene yields (~9% at 10% conversion) are higher than the propene yields on the same catalysts and at comparable conversions.

In spite of the complex character of the effect of the additives, some general observations can be made. Firstly, the selectivities to ethene are considerably higher (maximal values of ~85%) than the selectivities to propene (maximal values ~40%). Thus, the promoted VPO catalysts seem to be promising systems for the ODH of ethane, but not for the propane ODH. Moreover, the effect of the additives on the selectivity in the reactions of propane and ethane appears to be different and in several cases inverse. Thus, the Mo and higher amount of the La additives lead to the increase in the selectivity to propene, whereas they decrease the selectivity to ethene. Low content of the La additive gives rise to the increase in ethene selectivity and decrease in that to propene.

Higher selectivity to ethene, as compared with that to propene, can be ascribed to relatively high acidity of the VPO system [6–8]. It has been shown previously that the selectivity to propene in the ODH of propane increases with the decrease in the acidity of some vanadia based catalysts ( $\text{VO}_x\text{Al}_2\text{O}_3$ ,  $\text{VO}_x/\text{TiO}_2$ ), this decrease being induced by the introduction of alkali additives [10,11]. This effect has been explained by the decrease in the strength of bonding of propene to the catalyst surface on the alkali addition [20]: propene (considered as a base) is less strongly adsorbed on the less acidic surface and can easily desorb before undergoing further, consecutive surface reactions to undesirable carbon oxides. On the other hand, the ethene selectivity in the ODH of ethane on  $\text{VO}_x/\text{Al}_2\text{O}_3$  studied by López Nieto *et al.* [10] and  $\text{VO}_x/\text{SiO}_2$  [21] catalysts, is not affected by the alkali addition, *i.e.* by the acidity changes. López Nieto has pointed out [10] that the differences between propene and ethene selectivity may be due to the different basicity of the two olefins, sorption energy of ethene (less basic than propene), being less affected by the acidity of the catalyst surface.

Different basicity of the two olefins could also affect the rate of the reactions of electrophilic oxygen species  $\text{O}_2$ ,  $\text{O}_2^-$  and  $\text{O}^-$ , present on the surface during the oxidation reactions: according to Haber [22] such species may attack the double bond of an olefin and form peroxy and oxo species, which lead to total oxidation to  $\text{CO}_x$ .

Further studies are necessary to determine to what extent the additives to VPO system affect the acid-base properties and the distribution of oxygen species in the catalysts studied and to explain the different effect of the same addition (*e.g.* Mo and La) on the selectivity in the ODH of propane and ethane.

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