

## Effect of the Potassium Promoter Content in $V_2O_5/TiO_2$ Catalysts on Their Physicochemical and Catalytic Properties in Oxidative Dehydrogenation of Propane

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To optimize the content of the potassium promoter in  $V_2O_5/TiO_2$  system for oxidative dehydrogenation of propane ODH, the vanadia-titania catalysts of the potassium/vanadium (K/V) ratio ranging from 0.01 to 0.2 were obtained and tested in the title reaction. It has been found that the total rate of the propane consumption decreases considerably already on addition of small amounts of K (K/V = 0.01) to vanadia-titania system and only slightly at higher K content: its value is constant beginning from K/V = 0.05. The distinct increase in the selectivity to propene on addition of K is, on the other hand, observed at higher K content (K/V = 0.05–0.1). Addition of K to vanadia-titania catalysts leads to the decrease in acidity and increase in basicity of the system, as shown by measurements of the isopropanol decomposition, a probe reaction of acido-basic properties.

**Key words:** vanadia-titania catalysts: potassium promotion, oxidative dehydrogenation of propane

It has been found previously [1–3] that addition of potassium to  $V_2O_5/TiO_2$  catalysts at the K/V ratio equal 0.1 leads to the increase in selectivity to propene and decrease of that to carbon oxides in the oxidative dehydrogenation, ODH of propane. The latter reaction has attracted much interest in recent years [4–6] as a source of cheap propene for polymerization and selective oxidation processes. The increase in the selectivity to propene was accompanied by the decrease in the acidity and the increase in the basicity of the catalysts [1–3]. It was argued that, owing to the modification of the acido-basic properties, propene, formed in the first step of the ODH reaction, is easily desorbed before undergoing consecutive unfavourable reactions of total combustion [1–3].

In order to optimise the content of potassium, in the present work the  $V_2O_5/TiO_2$  catalysts containing different content of potassium in the range of the K/V ratio varying from 0.01 to 0.2 were synthesized and tested in the ODH of propane. The catalysts were characterized by the XPS technique and a model reaction of the isopropanol decomposition – a probe reaction for acido-basic properties [7,8].

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## EXPERIMENTAL

**Preparation of catalysts:** The  $V_2O_5/TiO_2$  catalysts were prepared by impregnation with aqueous solution of ammonium metavanadate at pH = 6 of a commercial anatase  $TiO_2$  support, evaporation of the solute, followed by drying for 12 h at 120°C and calcination under a flow of air for 5 h at 500°C. The K-doped samples were obtained by adding appropriate amounts of potassium nitrate to the metavanadate solution to obtain the desired K/V ratio. The support, product of Chemical Works, Police, Poland was washed thoroughly with hot water to remove potassium and phosphorus impurity. Its specific surface area, determined with BET method with krypton as a sorbate was 7 m<sup>2</sup>/g, XRD technique confirmed it to be pure anatase modification of  $TiO_2$ . The content of vanadia in the samples corresponded to 5 monolayers of  $V_2O_5$  (~ 4 wt %), calculated with the assumption that one monolayer contains 10 V atoms per 1 nm<sup>2</sup> of the support surface. The XRD analysis did not show the presence of crystalline  $V_2O_5$ . Earlier studies suggested that vanadia is present in the samples as partly amorphous  $V_2O_5$  and partly as polyvanadate surface groups  $(VO_x)_n$  attached to the anatase surface [3]. The specific area of the catalysts was, within the error of the BET method, the same as that of the  $TiO_2$  support. The symbols of the samples adopted further in the text are VTiKX where X = K/V ratio.

**XPS:** The XPS spectra were recorded with a VG Scientific ESCA-3 spectrometer using  $AlK\alpha_{1,2}$  radiation (1486.6 eV) from an X-ray source operating at 12 kV and 20 mA. The working pressure was better than  $2 \times 10^{-8}$  Torr (1 Torr = 133.3 Pa). The binding energies (BE's) were referenced to the C(1s) peak from the carbon surface deposit at 284.8 eV. The surface atomic ratios V/Ti and K/V were calculated with the procedure described in [9].

**Catalytic test:** Catalytic activity of the samples in oxidative dehydrogenation of propane was measured in a fixed bed flow apparatus at 330, 360 and 400°C. The reaction mixture contained 7 vol. % of propane in air, the constant flow of the reactants being maintained by mass flow controllers. 1 g of the samples were used in the experiments. The reactor (13 mm in diameter) was made of stainless steel, the thermocouple for the temperature measurements being placed coaxially in the catalyst bed. Analysis of products and unreacted propane was performed by on-line gas chromatography using Hewlett-Packard chromatograph with catharometric detection.  $C_3H_6$ , CO and  $CO_2$  were found as main reaction products, the amount of oxygenates (acrolein, acrylic acid) was below 1% of the total amounts of products. The samples were kept at a given temperature till a constant value of propane conversion and the yields of products were obtained (usually after 2–3 h). The carbon balance for conversions higher than about 10% was better than  $97 \pm 2\%$ . At lower conversions the balance was poorer and hence 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:

$$X_p = (c_p^\circ - c_p) / c_p^\circ,$$

where  $c_p^\circ$  and  $c_p$  are the concentrations of propane at the inlet and outlet of the reactor respectively. Pure  $TiO_2$  support was found inactive under the adopted conditions of the reaction, the conversion of propane at the highest temperature used (400°C) was below 1%.

**Isopropanol decomposition:** Decomposition of isopropanol, isoPrOH, to propene, acetone and di-isopropyl ether was studied at 170°C with the pulse method, using dried helium as a carrier gas. 0.1 g of the sample and 2  $\mu$ l pulses of isoPrOH were used, the total flow rate of helium being 30 ml/min. Analysis of products was performed with gas chromatography using Chromatron 18.3 apparatus with FID detection. The isoPrOH pulses were injected successively till constant values of conversion and amounts of products were attained (usually after 3–5 pulses). The amounts of products per 1 pulse reported further are the mean values obtained in 3 successive pulses after the stationary state of the activity was obtained. Before the experiments the samples were standardized in a stream of helium for 2 h at 200°C. The  $TiO_2$  support, used in the present studies yielded only trace amounts of products, the total conversion of isopropanol being less than 1%.

## RESULTS AND DISCUSSION

Table 1 presents the XPS data for the catalysts under study. BE values for V, Ti and O are not modified within the limits of experimental error by the addition of K and correspond to  $V^{5+}$  and  $Ti^{4+}$ . The major peak for O1s at  $530.4 \pm 0.2$  eV corresponds to the lattice oxygen in oxides, small peak at higher BE energy at  $532.9 \pm 0.2$  eV may be due to the surface OH groups. The BE of K is typical for  $K^+$  ion. The surface atomic ratio K/V increases with the total K content up to  $K/V = 0.05$  and remains practically constant at higher total K content. The latter fact suggests the change of the mode of K dispersion: at higher content potassium may be incorporated in the bulk of the samples, or it can form agglomerates of *e.g.*  $K_2O$ . The V/Ti ratio does not change significantly on addition of K up to  $K/V = 0.05$  and is higher at  $K/V = 0.1$ . The latter result indicates a better dispersion of the vanadia phase at higher K content.

**Table 1.** XPS data for K – doped  $V_2O_5/TiO_2$  catalysts.

Sample	VTi	VTiK0.01	VTiK0.02	VTiK0.05	VTiK0.1
	BE, FWHM	BE, FWHM	BE, FWHM	BE, FWHM	BE, FWHM
C1s	284.8 (2.5)	284.8 (2.4)	284.8 (2.4)	284.8 (2.4)	284.8 (2.3)
	286.8 (2.5)	287.8 (2.4)	287.9 (2.4)	287.3 (2.4)	287.3 (2.3)
				289.4 (2.4)	289.4 (2.3)
K2p	–	293.3 (2.3)	293.2 (2.3)	293.2 (2.5)	293.2 (2.2)
Ti2p	459.1 (2.2)	459.1 (2.0)	459.0 (2.1)	458.9 (1.9)	458.9 (1.9)
V2p	517.4 (2.8)	517.4 (2.6)	517.5 (2.5)	517.5 (2.6)	517.4 (2.4)
O1s	530.5 (2.3)	530.6 (2.2)	530.6 (2.2)	530.5 (2.1)	530.3 (2.2)
	533.1 (2.0)	532.8 (2.2)	532.8 (2.2)	533.1 (2.1)	532.9 (2.2)
V/Ti	0.272	0.271	0.277	0.260	0.369
K/V	0	0.08	0.16	0.27	0.28

BE, [eV] – binding energy, FWHM, [eV] – full width at half-maximum.

The same phenomenon was observed earlier [1,3] for  $V_2O_5/TiO_2$  and  $MoO_3/TiO_2$  catalysts promoted with higher amounts of alkali metals [ $Alk/V(Mo) = 0.1$ ]. Fig. 1 presents the total activity changes of the catalysts with the K/V ratio. The activity decreases sharply on introducing small amounts of K ( $K/V = 0.01$ ) and then only slightly with the further increase in the K content. It remains practically constant beginning from the K/V ratio equal 0.05. It can be observed that this practically constant value of the activity corresponds to the constant surface concentration of K observed in the XPS measurements. The decrease of the total activity indicates that potassium blocks the centres of the propane reactions with oxygen. Fig. 2 shows as an example the change of selectivities to different reaction products with the total conversion of propane for the VTiK0.02 catalyst at 330°C. Similar course of the selectivities was observed for other catalysts and other reaction temperatures. As seen the selectivity

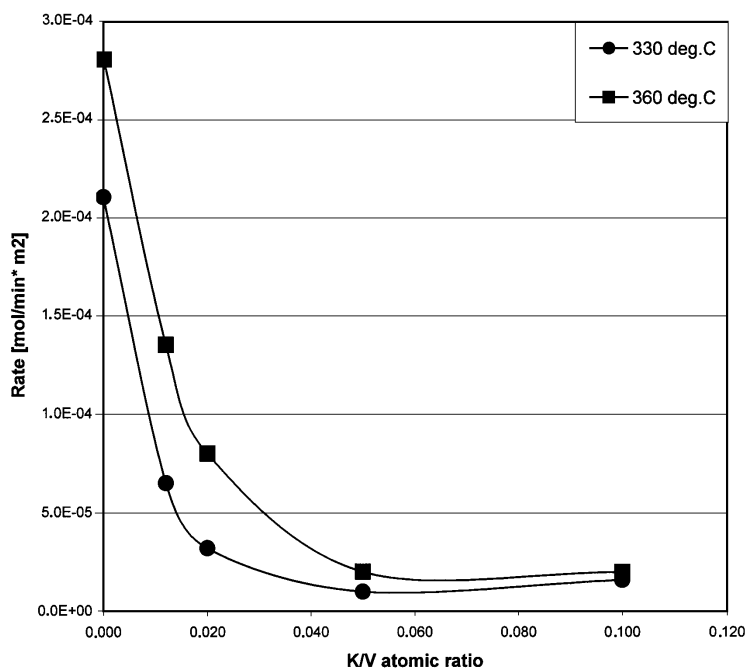


Figure 1. Rate of the propane consumption as a function of the potassium content.

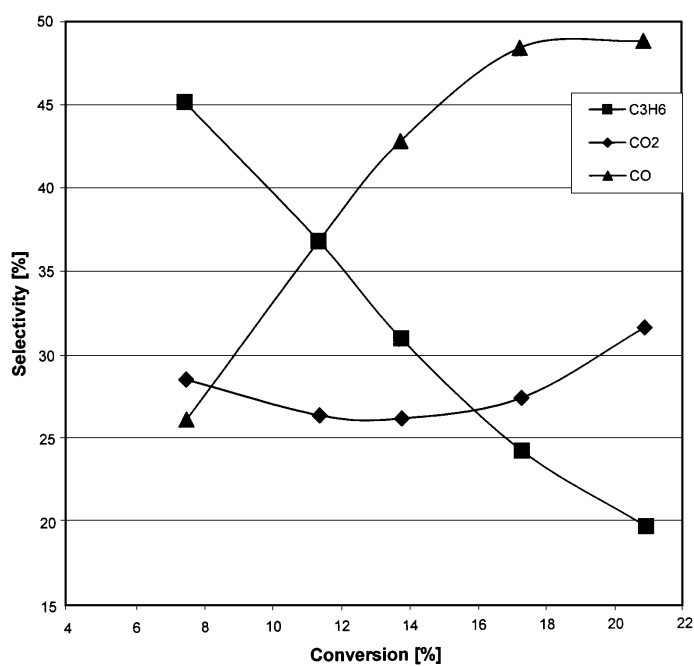


Figure 2. Selectivities to different reaction products as a function of the propane conversion for VTiK0.02 catalyst, 330°C.

to propene decreases with the increasing conversion in line with the parallel consecutive scheme of the ODH reactions [4–6], observed earlier also for the ODH of propane on vanadia-titania catalysts [10].

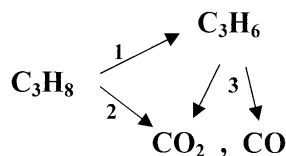


Table 2 summarises the initial selectivity data, estimated by extrapolation to the zeroth conversion of propane, which reflect the extent of parallel reactions 1 and 2 in reaction products formation. For the catalyst without K and those with small amounts of K up to  $K/V = 0.02$  both  $\text{CO}_2$  and CO are formed as primary products. Addition of K leads to a considerable decrease of the CO formation. For higher K content (catalyst KV0.05) this product is not formed at all by reaction 2. The changes of the initial selectivity to  $\text{CO}_2$  are smaller and, in contrast to CO,  $\text{CO}_2$  is formed as primary product even for the catalyst of higher K/V ratio 0.05. In Tab. 3 the selectivities to propene at 10% of propane conversion are compared for different reaction temperatures. For the VTiK0.1 and VTiK0.2 catalysts of the smallest activity, the conversions of 10% were obtained in the studied conditions only at  $400^\circ\text{C}$ . It follows from the data presented above that the extent of the effect of K on the selectivity to propene depends on the K content and on the reaction temperature. At 360 and  $400^\circ\text{C}$  the sequence of the selectivities to propene at comparable propane conversion is:



At  $330^\circ\text{C}$ :



The effect of potassium on the selectivity is clearly observed for the higher K content ( $K/V = 0.05$ ). The ratio  $K/V = 0.05\text{--}0.1$  appears then optimal for the high selectivity to propene.

**Table 2.** Initial selectivity to different reaction products in ODH of propane on K – doped  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts.

Catalysts	S [%]								
	330°			360°			400°		
	$\text{C}_3\text{H}_6$	CO	$\text{CO}_2$	$\text{C}_3\text{H}_6$	CO	$\text{CO}_2$	$\text{C}_3\text{H}_6$	CO	$\text{CO}_2$
VTi	55	25	20	65	20	18	50	20	30
VTiK0.01	–	–	–	65	10	20	–	–	–
VTiK0.02	60	8	28	70	8	20	–	–	–
VTiK0.05	80	0	20	85	0	10	87	0	15
VTiK0.1	–	–	–	87	0	10	85	0	13
VTiK0.2	–	–	–	88	0	11	86	0	14

**Table 3.** Selectivity to different reaction products at 10% propane conversion in ODH of propane on K-doped V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts.

Catalysts	S [%]								
	330°			360°			400°		
	C <sub>3</sub> H <sub>6</sub>	CO	CO <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	CO	CO <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	CO	CO <sub>2</sub>
VTi	40	405	20	38	41	218	39	40	21
VTiK0.01	36	39	26	43	34	23	–	–	–
VTiK0.02	41	33	27	43	33	24	–	–	–
VTiK0.05	52	28	21	57	24	19	59	24	18
VTiK0.1	–	–	–	–	–	–	58	22	20
VTiK0.2	–	–	–	–	–	–	56	24	20

Table 4 presents the data of the isopropanol decomposition on some of the catalysts studied. As seen, the amounts of propene and di-isopropyl ether – which characterise the acidity (the number of acid centres) – decrease steadily with the increase of the potassium content to K/V = 0.1 and only slightly at higher K/V ratio. The basicity of the catalysts (the amount of acetone and acetone/propene ratio) increases similarly with the K content. The latter data confirm earlier findings [1–3], which have shown that K decreases the number of the acid centres and modifies the basicity. These changes can be correlated with the increase in the selectivity to propene: low acidity and high basicity favour desorption of a propene molecule (of basic, or nucleophilic character) to the gas phase, thus preventing it from the consecutive total combustion to CO<sub>x</sub>.

**Table 4.** Isopropanol decomposition on V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts with different amounts of K [test of acid – base properties].

Sample	K/V	DIE*	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub> O
				(acetone)
10 <sup>6</sup> mol m <sup>-2</sup> sec <sup>-1</sup>				
VTi – O	0	0.30	1.6	1.2
VTiK – 0.05	0.05	0.23	0.7	1.8
VTiK – 0.1	0.1	0.17	0.4	2.1
VTiK – 0.2	0.2	0.14	0.3	2.0

Reaction temp. 170°C, pulse technique. 2 μl isopropanol in He (30 ml/min), 0.1 g sample.

\* DIE-di-isopropyl ether.



