

V₂O₅-ZrO₂ catalyst for selective oxidation of *o*-xylene to phthalic anhydride: I. Catalyst preparation, catalytic activity and selectivity measurements

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The thermal stability, activity and selectivity of a series of V₂O₅-ZrO₂ catalyst samples towards *o*-xylene oxidation to phthalic anhydride have been investigated. It has been established that the phthalic anhydride content yield reaches about 55 mol.% in samples containing 7 and 10 wt.% V₂O₅. The selectivity of the catalyst with 7 wt.% V₂O₅-ZrO₂ has been compared to that of commercially available V₂O₅-TiO₂ (anatase). The investigations have been performed within two temperature ranges. At low temperatures (below 410°C) the V₂O₅-TiO₂ (anatase) catalyst shows a better selectivity to phthalic anhydride than the V₂O₅-ZrO₂ catalyst does. At high temperatures, the V₂O₅-ZrO₂ catalyst is more selective with respect to the main product of partial oxidation due to the positive effect of the ZrO₂ support. Even when the temperature rises up to 550°C and the time of exploitation becomes 50 h, the selectivity of V₂O₅-ZrO₂ decreases slightly and remains above 50 mol.%, whereas with the V₂O₅-TiO₂ (anatase) sample a significant decrease in selectivity (below 45 mol.%) is observed. The results from experiments on the activity and selectivity of a model mixture of 7 wt.% V₂O₅-ZrO₂ and pure ZrO₂ taken in a ratio of 1:1 show that high catalyst selectivity is achieved when the zirconia surface is completely covered by VO_x-phases. Studies by different physicochemical analysis methods have shown that V₂O₅-ZrO₂ used in a high-temperature regime undergoes no significant phase and structural changes, which is an indication of its good thermal stability. The specific surface area decreases a little, the monoclinic zirconia support exhibits no phase changes and the fine structure of the V₂O₅ active phase displays no substantial alterations.

Key words: V₂O₅-ZrO₂ catalyst, V₂O₅-TiO₂ (anatase) catalyst, partial selective oxidation, *o*-xylene oxidation, phthalic anhydride, maleic anhydride.

INTRODUCTION

Vanadium oxide catalysts are frequently used for the oxidation of aromatic compounds [1, 2]. As the specific surface area and catalytic activity are usually low, the active phase is fixed on a support. The role of the support is not only to increase the surface area and to improve the mechanical strength. It might also modify the active surface due to an interaction of the support and the active phase. Among the multitude processes of partial oxidation of aromatic compounds, the process of oxidation of *o*-xylene is most interesting both in scientific and industrial aspects. Usually such catalysts are supported on TiO₂ in the form of anatase [3] and SiO₂ [2]. In comparison with titanium and silica, much less attention has been paid to zirconium as a support. In our opinion the use of zirconia is interesting because of its high thermal stability and acid-base character, which is very close to that of TiO₂. Having in mind that the process of partial oxidation is highly exothermic, these properties of the support are of great significance. In the scientific and patent literature there are few communications concerning

the use of ZrO₂ as a support of vanadium oxide catalysts for partial oxidation of *o*-xylene. There are no published data regarding the selectivity of V₂O₅-ZrO₂ catalysts to the valuable side product, maleic anhydride, as well as to the undesired substance phthalide.

Supported metal oxides exhibit interesting catalytic properties depending on the kind of the support, the active component content and the preparation method [5–7]. In particular, vanadium oxide catalysts combined with various promoters are widely used for several reactions including oxidation of hydrocarbons [8], ammoxidation of aromatics and methylaromatics [9], olefins [10], ethanol and ethane, ammoxidation of 3-picoline and toluene, oxidation of methanol [11] and selective catalytic reduction of NO_x by NH₃ [12, 13].

All partial oxidation processes are highly exothermic, due to which the support of the V₂O₅ active component should be carefully chosen. Among the mentioned partial oxidation processes and oxidation ammonolysis, the partial oxidation of *o*-xylene to phthalic anhydride is most interesting both from industrial and scientific viewpoint [5, 6, 14]. The V₂O₅-TiO₂ (anatase) system is the basis of modern catalysts for partial oxidation of *o*-xylene to phthalic

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anhydride [5, 14].

It has been established [23, 24] that under the effect of high temperatures and reduction medium the catalyst is sintered, and the anatase is transformed into rutile, part of the V^{4+} ions being incorporated in the rutile lattice [15], which leads to sharply dropping of the catalyst activity. This deactivation is observed mostly in the 'hot spot' zone of the industrial reactor where the temperature exceeds 440°C and where the largest part of the reaction proceeds [16]. These investigations show that it is very important to find supports that would be stable at high temperatures in a reduction medium.

During the past years some patents have reported the use of ZrO_2 as a support of V_2O_5 . Systems V_2O_5 - ZrO_2 in combination with various promoters are widely used for several reactions including *o*-xylene oxidation [17, 18], ammoxidation of aromatics and methylaromatics, oxidation of toluene [19, 20], decomposition of propan-2-ol [21, 22], oxidative dehydrogenation of propane [23, 24], oxidation of naphthalene, partial oxidation of methanol [25] and selective catalytic reduction of NO_x by C_3H_6 [26]. The utilisation of ZrO_2 is based on the fact that it is stable at very high temperatures [27] and its acid-basic characteristics are very close to those of TiO_2 .

Interesting studies [27, 28–33] have reported the use of zirconia as a support of vanadium oxide catalysts. The valuable zirconia properties in this aspect are its high thermal stability and acid-basic characteristics which are close to those of titania (anatase) [28–30].

It is known [34] that vanadia promotes the transition of tetragonal to monoclinic zirconia at high temperatures. The interaction of dispersed vanadium oxide species with a zirconia support leads to the formation of ZrV_2O_7 . Antimony tends to stabilise the tetragonal phase of zirconia and its specific area. The simultaneous presence of Sb and V on zirconia at 1 cm coverage leads to a preferential interaction of individual V and Sb oxides on the zirconia surface rather than the formation of a binary Sb-V oxide. However, at high Sb-V coverage, $SbVO_4$ is formed at the expense of surface Sb oxide, while the transition to monoclinic polymorph is minimised. Simultaneously, the excess of antimony forms α - Sb_2O_4 .

In previous papers [35, 36], the selectivity of supported V_2O_5 - ZrO_2 catalysts for *o*-xylene oxidation to phthalic anhydride was investigated under conditions close to the industrial ones with conventional supported V_2O_5 - TiO_2 (anatase) oxide catalysts. The by-products of this oxidation process were maleic anhydride, phthalide and the combustion products – CO and CO_2 . In contrast to

conventional V_2O_5 - TiO_2 (anatase) catalysts, the V_2O_5 - ZrO_2 catalysts exploited at low oxidation temperatures (310 – 350°C), were found to be very selective to the valuable by-product maleic anhydride, but showed no selectivity to the harmful organic oxidation products. The same catalyst also demonstrated a relatively high selectivity towards the main product of oxidation (phthalic anhydride) and a very low selectivity to the undesired phthalide formed during the oxidation. The data designated brought to assumption [34] that a supported V_2O_5 - ZrO_2 catalyst may be used for selective oxidation of *o*-xylene. This catalyst should be combined with the conventional V_2O_5 - TiO_2 (anatase) catalysts and placed in the low-temperature zone of the industrial reactor.

The goal of the present investigation was to prepare a V_2O_5 - ZrO_2 catalyst, to study its catalytic activity and selectivity for partial *o*-xylene oxidation towards phthalic anhydride and to compare our results with the conventional V_2O_5 - TiO_2 (anatase) catalyst.

EXPERIMENTAL

Synthesis method of the catalyst

Supported V_2O_5 - ZrO_2 catalyst samples were obtained by a method based on the preparation of an industrial BASF catalyst: V_2O_5 (specific surface area – $6\text{ m}^2/\text{g}$) and NH_4VO_3 (AG-Fluka) were used for V^{5+} -contention; ZrO_2 was taken as a commercial product (AG-Fluka; monoclinic [9], specific surface area – $26\text{ m}^2/\text{g}$).

The catalyst samples were prepared by reducing V^{5+} of V_2O_5 . The ratio $V_2O_5:H_2C_2O_4 = 1:(2.5\text{--}3.0)$ in an aqueous solution of oxalic acid at 60 – 80°C . Zirconia was introduced simultaneously. Surfactants (formamide or diphenylformamide in an aqueous solution at ratios water:formamide = 3.5 – $5.0:1.0$) were used as binding substances. The suspension obtained was subjected to ultrasonic treatment with a view to homogenisation, dispersion and additional activation of the catalyst mass. The active catalyst mass was applied on an inert support (steatite spheres, 6 mm in diameter), by pulverising the suspension on the spheres pre-heated up to 200 – 250°C . The catalyst samples thus obtained had a coverage layer of the total catalyst mass with 1 mm thickness. They were dried at 110°C and calcined for 2 – 10 h at 450°C (a temperature corresponding to the calcination temperature of the industrial V_2O_5 - TiO_2 (anatase) catalyst in air flow).

Catalytic activity and selectivity measurement

The activity and selectivity of the catalyst

samples for the vapour-phase partial oxidation of *o*-xylene to phthalic anhydride were investigated in a standard flow-type installation functioning at a pressure of 1 atm. The laboratory flow reactor had a length of 450 mm and contained 250 cm³ catalysts. It was immersed in a salt bath containing $KNO_2:NaNO_2$ (1:1) salt melt, the temperature being maintained with an accuracy of up to 1°C. The temperature of the catalyst grains along the catalyst layer was measured by thermocouples. A minipump achieved the exact dosage of *o*-xylene. Along with the air introduced by a compressor, *o*-xylene came to a mixer with a filling where the temperature of the air-xylene mixture was maintained at 180°C.

Characterisation of catalysts and products of o-xylene oxidation

The analysis of the oxidation products was performed on-line by a gas chromatograph. The contents of phthalic anhydride (FA), phthalide (Ft), benzoic acid (BA), maleic anhydride (MA), CO_x – ($CO_2 + CO$) were determined. The catalyst samples were activated by air for 48 hours, while the selectivity measurements were done 2 h after fixing the corresponding regime. In all experiments a 100% *o*-xylene conversion was achieved.

The final reaction mixture was subjected to gas-chromatographic analysis in a Perkin Elmer 8500 apparatus (capillary column OV-101, $l = 25$ m, inner diameter = 0.25 mm, carrier gas H_2 , $T = 90$ – $120^\circ C$, detector PID). The reaction products found were *o*-toluyl aldehyde, benzoic acid, phthalide, maleic anhydride, phthalic anhydride and unreacted *o*-xylene. The products of full oxidation to CO and CO_2 were determined chromatographically in a steel column ($l = 4$ m, 1/8", GMCS, 60–80 mesh, hot catarometer as a detector).

The catalyst samples were activated in an air flow at the corresponding temperature and volume rate for 48 h. The kinetic measurements were performed two hours after establishing the corresponding regime.

RESULTS AND DISCUSSION

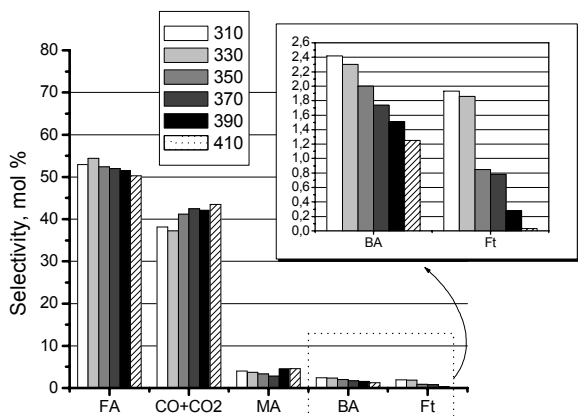
Catalytic activity and selectivity

Catalyst V_2O_5 - ZrO_2 samples with 4, 7 and 10% of the active V_2O_5 component content were prepared. In the conventional V_2O_5 - TiO_2 (a) catalyst the active component is usually between 2 and 10%. In order to determine the qualities of the synthesised V_2O_5 - ZrO_2 catalyst samples, differing in the amount of deposited V_2O_5 , we carried out test in the temperature interval 310–410°C, under flow rates of

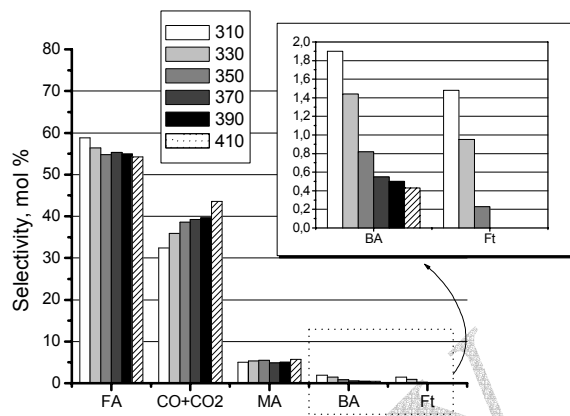
1500–2500 h⁻¹. These conditions are close to the industrial ones of exploitation of the conventional V_2O_5 - TiO_2 (a) catalysts. The experimental results of activity and selectivity and studies of several V_2O_5 - ZrO_2 catalyst samples are exposed in Figs. 1–3. It can be seen that the catalytic sample with 7% V_2O_5 content has the best selectivity towards phthalic anhydride exposed at the temperatures 350, 370 and 390°C and space velocity $w = 2000$ h⁻¹, but in the case of $T = 350^\circ C$ the by-products content (BA and Ft) becomes higher.

The poorest selectivity has been found for the sample with lowest (4%) amount of supported V_2O_5 (Fig. 1). This difference reaches about 15% at temperatures higher than 350°C and is preserved even at the highest temperatures. The fact observed clearly shows the specific promoting effect of ZrO_2 . These results are especially interesting having in mind that the highest selectivity to phthalic anhydride is produced by a V_2O_5 - ZrO_2 catalyst sample containing 7 wt.% V_2O_5 , which contents is much higher than that of a monolayer coverage (about 3 wt.% V_2O_5). On the other hand, it is well known [6] that a V_2O_5 - ZrO_2 catalyst having monolayer coverage shows highest selectivity to phthalic anhydride.

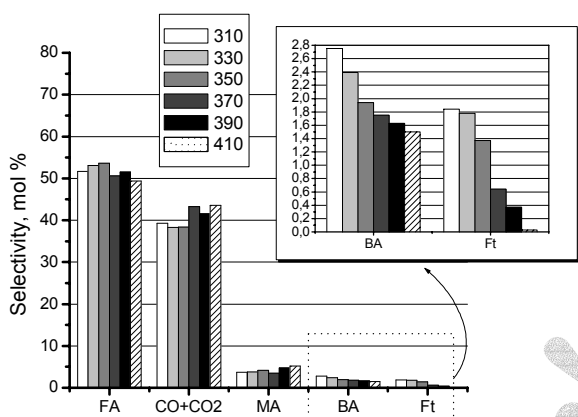
As to the selectivity to the valuable side product of oxidation – maleic anhydride (MA), the highest values have been obtained by the sample possessing the highest (10 wt.%) V_2O_5 , while the samples of lowest V_2O_5 content show again the lowest selectivity to maleic anhydride (Figs. 1–3). It is worth noting that the highest selectivity (about 6 mol.%) is established not only at low temperature regime 310–350°C, but also at high temperature (450°C) under all flow rates. The promoted industrial V_2O_5 - TiO_2 (a) catalyst, depending on the exploitation conditions, shows a lower selectivity to maleic anhydride (in the range of 2–5 mol.%). The high selectivity to maleic anhydride demonstrated by the V_2O_5 - ZrO_2 catalyst in all the temperature range is a good basis to optimise the process of partial oxidation of *o*-xylene. For example, a part of the conventional V_2O_5 - TiO_2 (a) catalyst operating in the spot zone can be replaced by V_2O_5 - ZrO_2 catalyst. It is also of scientific and technological interest the V_2O_5 - ZrO_2 catalyst to be promoted in order to raise its total selectivity to phthalic and maleic anhydrides. As can be seen in Figs. 1 and 3, a minimum of the selectivity to maleic anhydride is observed at temperatures about 370°C for the catalyst samples containing 4 and 10 wt.% V_2O_5 . We are not able to explain satisfactorily this fact at present, but it is probably due to the specific promoting effect of ZrO_2 .



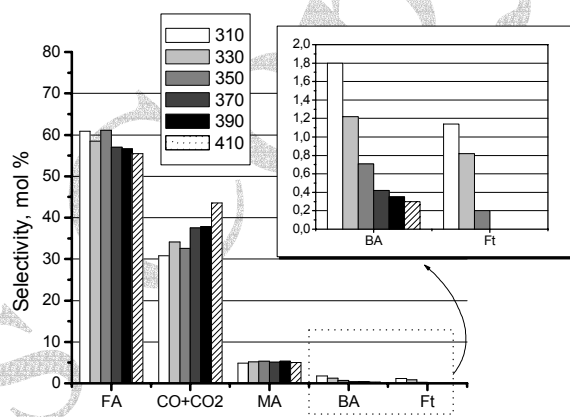
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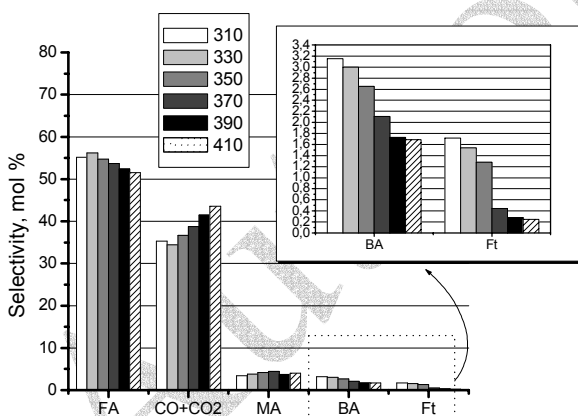
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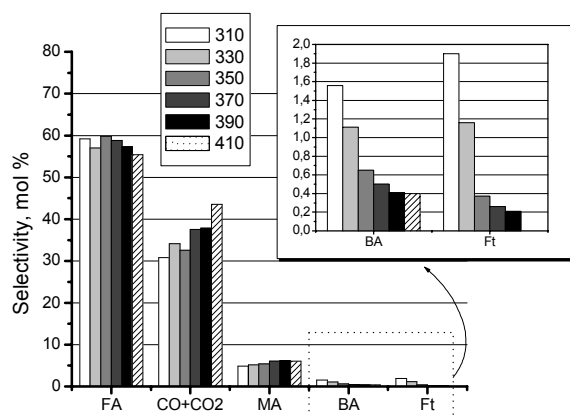
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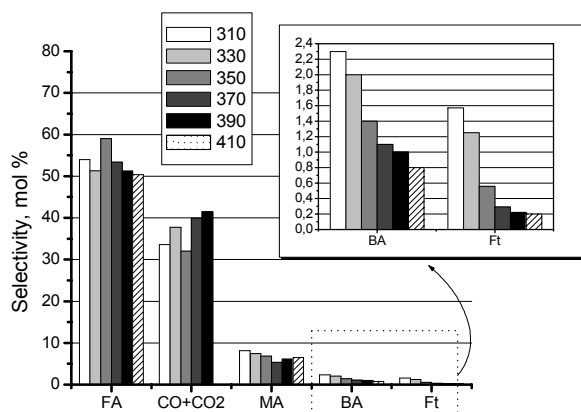
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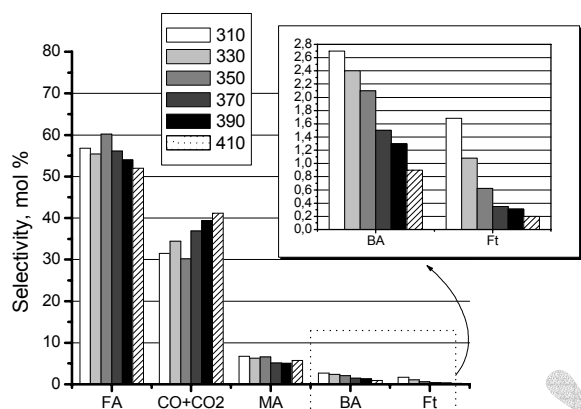
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Fig. 1. Oxidation of *o*-xylene over 4% V_2O_5 - ZrO_2 catalyst. Product selectivity (S_i) obtained for steady state at different temperatures ($T = 310, 330, 350, 370, 390$ and 410°C) and different volume rates: a – $w = 1500 \text{ h}^{-1}$, b – $w = 2000 \text{ h}^{-1}$, c – $w = 2500 \text{ h}^{-1}$; initial concentration of *o*-xylene – $C_{\text{xylene}} = 42 \text{ g/nm}^3$.

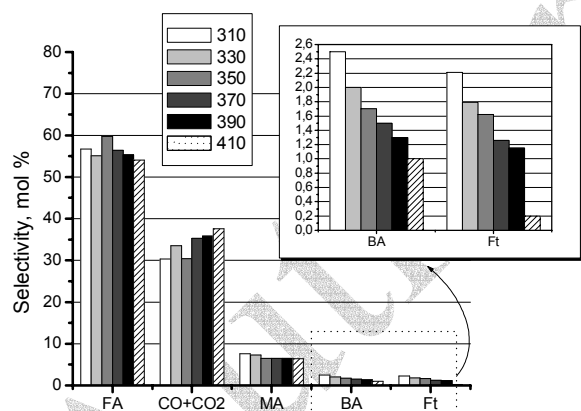
Fig. 2. Oxidation of *o*-xylene over 7% V_2O_5 - ZrO_2 catalyst. Product selectivity (S_i) obtained for steady state at different temperatures ($T = 310, 330, 350, 370, 390$ and 410°C) and different volume rates: a – $w = 1500 \text{ h}^{-1}$, b – $w = 2000 \text{ h}^{-1}$, c – $w = 2500 \text{ h}^{-1}$; initial concentration of *o*-xylene – $C_{\text{xylene}} = 42 \text{ g/nm}^3$.



a



b

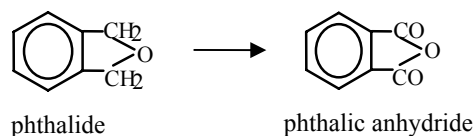


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Fig. 3. Oxidation of *o*-xylene over 10% V_2O_5 - ZrO_2 catalyst. Product selectivity (S_i) obtained for steady state at different temperatures ($T = 310, 330, 350, 370, 390$ and 410°C) and different volume rates: a – $w = 1500 \text{ h}^{-1}$, b – $w = 2000 \text{ h}^{-1}$, c – $w = 2500 \text{ h}^{-1}$; initial concentration of *o*-xylene – $C_{\text{xylene}} = 42 \text{ g/nm}^3$.

As to the selectivity of the undesired intermediate product of partial oxidation phthalide (Ft) and benzoic acid (BA), it is heighten for the samples with 4 and 10 wt.% V_2O_5 and decreases sharply as a function of the temperature for all catalyst samples tested (Figs. 1 and 3). Having in mind that the catalyst V_2O_5 - ZrO_2 sample with 7 wt.% V_2O_5 shows highest selectivity (Fig. 2) to phthalic anhydride at

all flow rates and temperatures, it may be concluded that the phthalide is an intermediate oxidation product. It is oxidised to phthalic anhydride like in the presence of V_2O_5 - TiO_2 (a) catalyst.



The selectivity to the products of destructive oxidation CO and CO_2 increases significantly (10–15 mol.%) (Figs. 1–3) with temperature for all catalyst compositions and all flow rates. It is remarkable that under highest flow rate ($w = 2500 \text{ h}^{-1}$) all catalyst samples show very close selectivity values to CO and CO_2 over the whole temperature range. Taking into account the almost constant catalyst activity to phthalic anhydride at 350°C , one may settle that the increase of the products of destructive oxidation (CO , CO_2) as a function of the temperature can be ascribed to the direct combustion of a part of *o*-xylene, but not of phthalic anhydride.

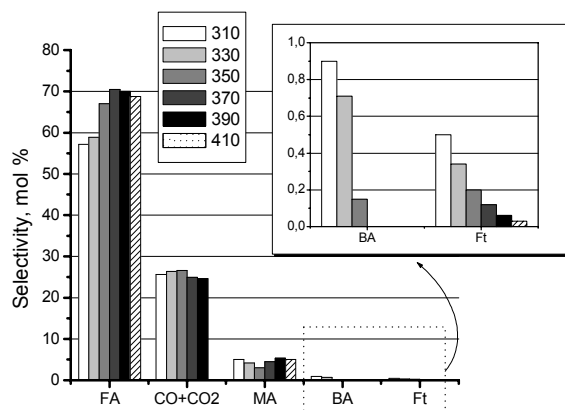
Comparison between 7% V_2O_5 - ZrO_2 and 7% V_2O_5 - TiO_2 catalysts

Figure 4 presents the main products of *o*-xylene oxidation - FA, MA, Ft, BA and CO_x , the selectivity of *o*-xylene oxidation towards the different reaction products as a function of temperature (310–410°C) and space velocity ($w = 1500$ – 2500 h^{-1}) for a catalyst sample of 7 wt.% V_2O_5 - TiO_2 (anatase). This composition exposes the best catalytic properties – a fact, well known from scientific papers.

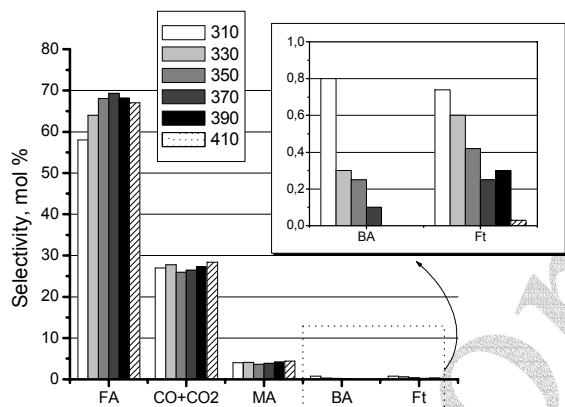
At a temperature rising from 310 to 370°C , the selectivity increases up to about 10%. The further temperature rising to 390 and 410°C leads to slight decrease in selectivity.

Simultaneously, the undesired product of not complete oxidation (phthalide) decreases significantly in amount. The temperature effect on the selectivity towards of over-oxidised products (maleic anhydride, carbon oxide and carbon dioxide) towards oxidation is different. The selectivity to maleic anhydride exhibits a minimum at 350°C under all three volume rates, whereas the selectivity towards oxidation to carbon monoxide and carbon dioxide is constant over the whole temperature range (310– 410°C) and is independent of the space velocity. According to the experimental results, the catalytic studies at higher temperatures when the amount of partial oxidation product (phthalide) is small, while the amount of the desired product of *o*-xylene oxidation (phthalic anhydride) increases, are more interesting. However, it is well known [1] that V_2O_5 - TiO_2 (anatase) catalysts are strongly deac-

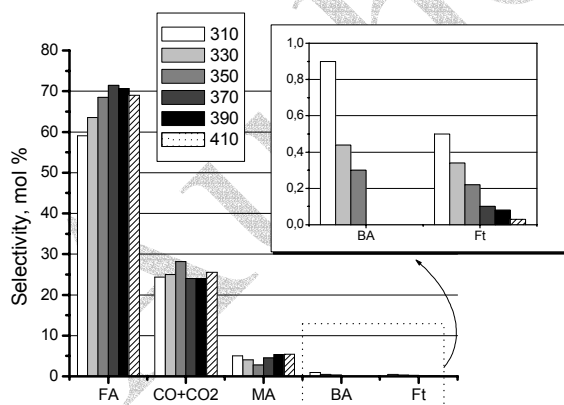
tivated at high temperatures ($> 440^\circ\text{C}$). For that reason we also investigated V_2O_5 - ZrO_2 catalysts which are expected to have a higher thermal stability and are very close to V_2O_5 - TiO_2 (anatase) catalysts with respect to their acid-base characteristics.



a



b



c

Fig. 4. Oxidation of *o*-xylene over 7% V_2O_5 - TiO_2 catalyst. Product selectivity (S_i) obtained for steady state at different temperatures ($T = 310, 330, 350, 370, 390$ and 410°C) and different volume rates: a – $w = 1500 \text{ h}^{-1}$, b – $w = 2000 \text{ h}^{-1}$, c – $w = 2500 \text{ h}^{-1}$; initial concentration of *o*-xylene – $C_{\text{xylene}} = 42 \text{ g/nm}^3$.

It is obvious that the selectivity increases with the reaction temperature although this increase is

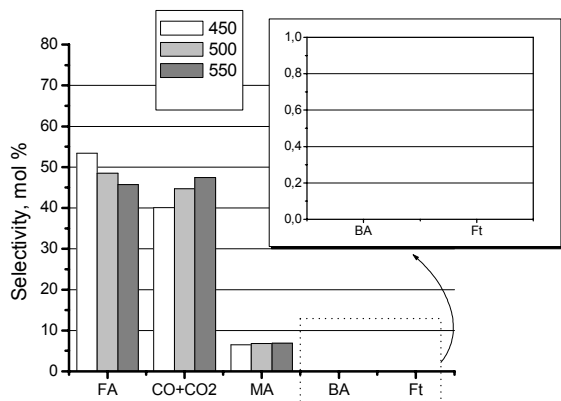
smaller than that for the V_2O_5 - TiO_2 (anatase) catalyst (Fig. 4). With temperature raising the amount of the partial oxidation product considerably decreases and is practically independent of the space velocity. As to the over-oxidised products (maleic anhydride, carbon monoxide, carbon dioxide), their amount increases with temperature. Comparison with the V_2O_5 - TiO_2 (anatase) catalyst shows that 7% V_2O_5 - ZrO_2 catalyst samples (Fig. 2) display a 5–15% higher selectivity with respect to carbon monoxide oxidation. These experimental results indicate that at low oxidation temperatures (310 – 410°C), V_2O_5 - TiO_2 (anatase) catalysts have a much higher selectivity towards *o*-xylene oxidation to phthalic anhydride than in the case of the V_2O_5 - ZrO_2 catalyst.

The similar catalytic behaviour of the both compared samples was an expected result. The reason is probably in the similar structures of the supports (ZrO_2 and TiO_2) and the active component of V_2O_5 .

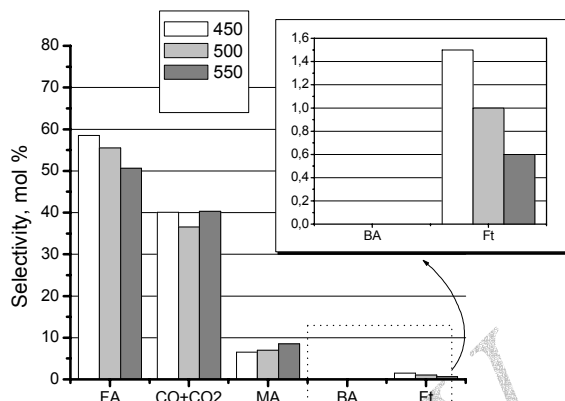
During industrial catalytic exploitation, the accidental deviation of the normal technology regime is an often case. It is really possible the transcendent temperature rises to act destructively towards the catalyst. In order to check the thermal stability of our catalyst an additional experiment was carried out – to compare the selectivity of both samples in a temperature range of 450 – 550°C . Those temperatures are much higher over the normal ones for the standard V_2O_5 - TiO_2 (anatase) catalysts. The resulting selectivity after 10 h exploitation in overheated regime towards the main products of *o*-xylene oxidation – FA, MA, Ft, BA and CO_x over the V_2O_5 - ZrO_2 catalyst are shown in Fig. 5 and over V_2O_5 - TiO_2 (anatase) – in Fig. 6. In this case the selectivity towards the main oxidation product FA is comparable (55 mol.%). BA and Ft are not present in V_2O_5 - ZrO_2 probes and Ft is about 1.4% Ft in the V_2O_5 - TiO_2 (anatase) sample. Probably the high-temperature regime had an influence over the V_2O_5 - TiO_2 (anatase) catalyst with resulting structural and morphologic changes and the sintering processes led to catalyst deactivation.

The thermal stability of V_2O_5 - ZrO_2 and the conventional V_2O_5 - TiO_2 (anatase) sample was investigated after their prolonged (up to 50 h) exploitation at high temperature (500°C). The comparative results are shown in Figs. 7 and 8.

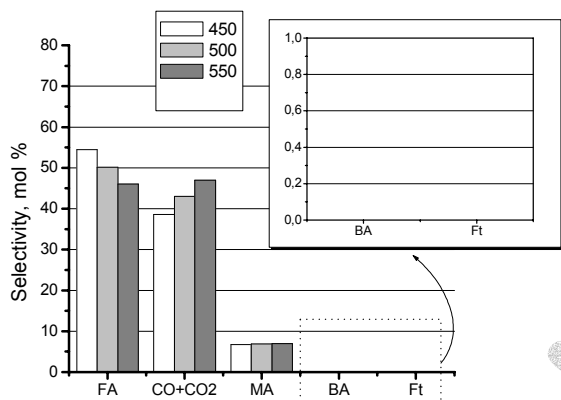
The change in the catalytic selectivity behaviour after their long-time high-temperature treating exposes the main predominance of the V_2O_5 - ZrO_2 catalyst. In order to illustrate this one can compare the changes in V_2O_5 - TiO_2 (anatase) samples in Figs. 4 and 8 and V_2O_5 - ZrO_2 (anatase) samples – in Figs. 2 and 7.



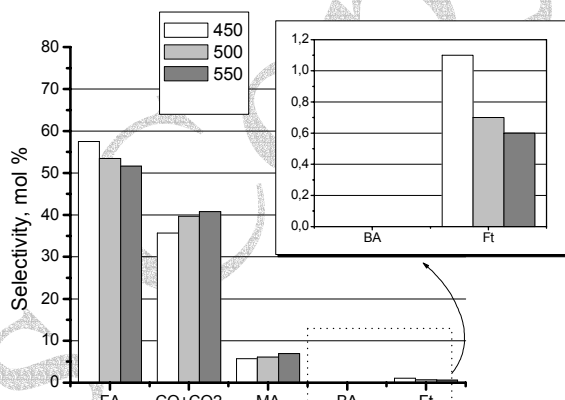
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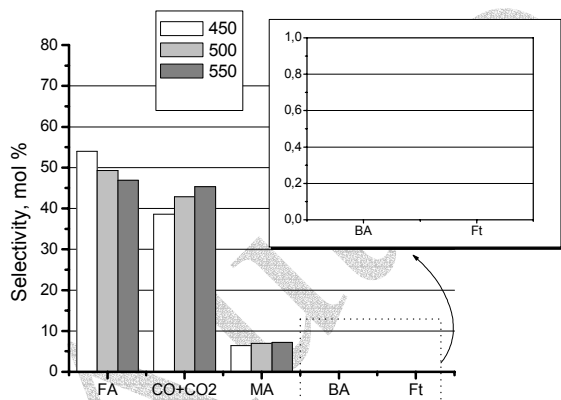
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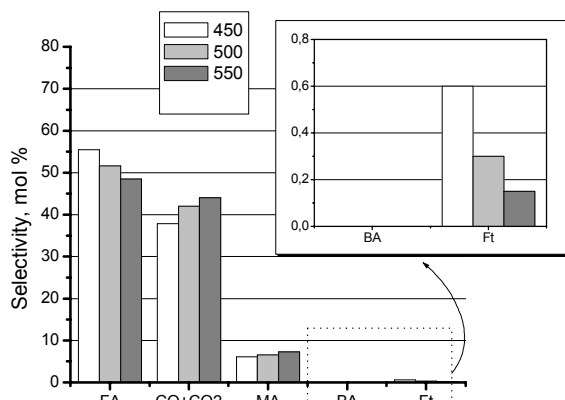
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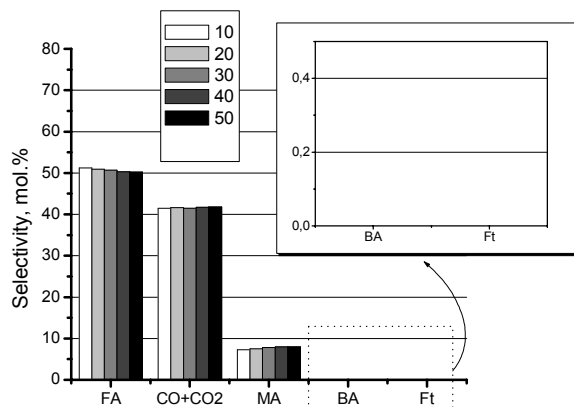
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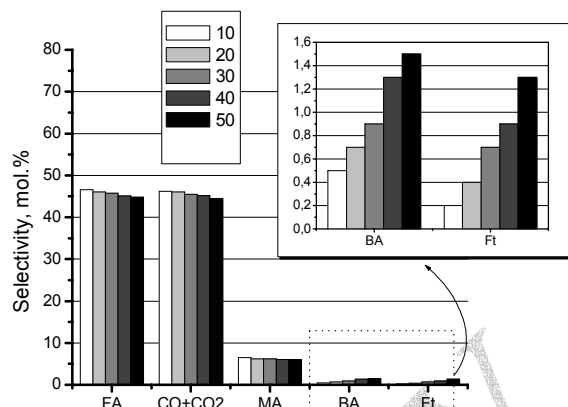
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Fig. 5. Oxidation of *o*-xylene over 7% V_2O_5 - ZrO_2 catalyst. Product selectivity (S_i) obtained for steady state at different temperatures ($T = 450, 500$ and 550°C) and different volume rates: a – $w = 1500 \text{ h}^{-1}$, b – $w = 2000 \text{ h}^{-1}$, c – $w = 2500 \text{ h}^{-1}$; initial concentration of *o*-xylene – $C_{\text{xylene}} = 42 \text{ g/nm}^3$.

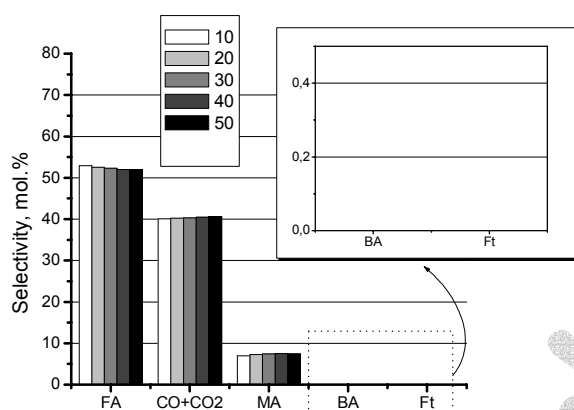
Fig. 6. Oxidation of *o*-xylene over 7% V_2O_5 - TiO_2 catalyst. Product selectivity (S_i) obtained for steady state at different temperatures ($T = 450, 500$ and 550°C) and different volume rates: a – $w = 1500 \text{ h}^{-1}$, b – $w = 2000 \text{ h}^{-1}$, c – $w = 2500 \text{ h}^{-1}$; initial concentration of *o*-xylene – $C_{\text{xylene}} = 42 \text{ g/nm}^3$.



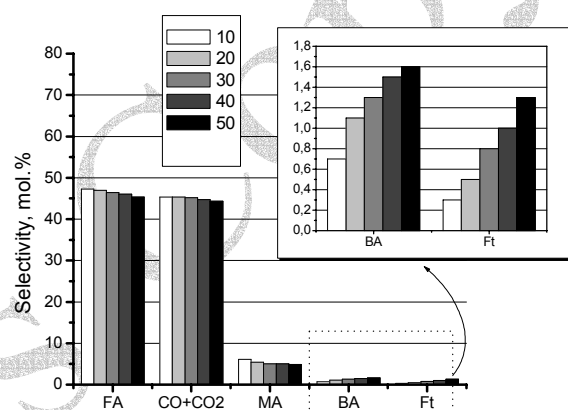
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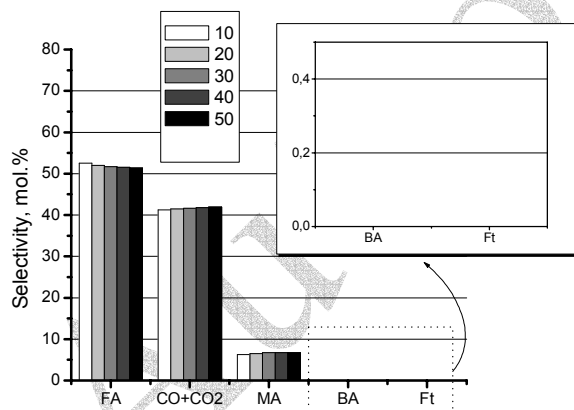
a



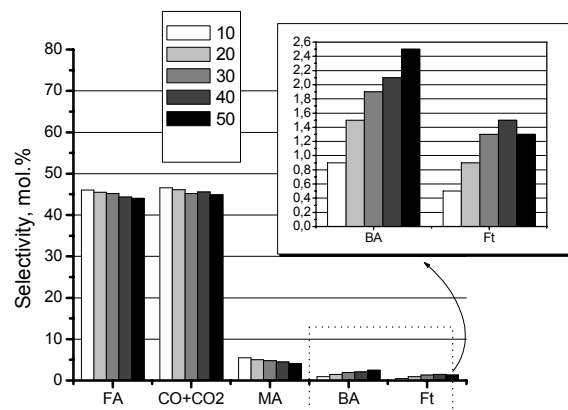
b



b



c



c

Fig. 7. Oxidation of *o*-xylene over 7% V_2O_5 - ZrO_2 catalyst. Product selectivity (S_i) obtained for steady state ($T = 500^\circ\text{C}$) at different times exploitation ($\tau = 10, 20, 30, 40$ and 50 h) and different volume rates: a – $w = 1500 \text{ h}^{-1}$, b – $w = 2000 \text{ h}^{-1}$, c – $w = 2500 \text{ h}^{-1}$; initial concentration of *o*-xylene – $C_{\text{xylene}} = 42 \text{ g/nm}^3$.

Fig. 8. Oxidation of *o*-xylene over 7% V_2O_5 - TiO_2 catalyst. Product selectivity (S_i) obtained for steady state ($T = 500^\circ\text{C}$) at different times exploitation ($\tau = 10, 20, 30, 40$ and 50 h) and different volume rates: a – $w = 1500 \text{ h}^{-1}$, b – $w = 2000 \text{ h}^{-1}$, c – $w = 2500 \text{ h}^{-1}$; initial concentration of *o*-xylene – $C_{\text{xylene}} = 42 \text{ g/nm}^3$.

The selectivity of V_2O_5 - TiO_2 (anatase) samples to the main product FA drops sharply from 72 mol.% (Fig. 4) to 43 mol.% (Fig. 8). The selectivity to the total oxidation product (CO_x) rises twice—from 27 mol.% (Fig. 4) to 45 mol.% (Fig. 8). The maleic anhydride contents stand almost unchanged after pre-heating, since the undesirable by-products contents significantly rise: BA content increases from 0.9 mol.% (Fig. 4) to 2.5 mol.% (Fig. 8) and Ft- from 0.01 mol.% (Fig. 4) to 1.3 mol.% (Fig. 8). During the exploitation time the Ft and BA content increase proportionally with pre-heating from 10 to 50 h.

The selectivity of V_2O_5 - ZrO_2 samples to the main product FA decrease slightly from 63 mol.% (Fig. 2) to 51 mol.% (Fig. 7). The selectivity to the total oxidation product (CO_x) stands almost unchangeable and varies about 40 mol.%. The maleic anhydride contents increase from 5 mol.% (Fig. 2) to 8 mol.% (Fig. 7). The undesirable by-products BA and Ft are not registered at high temperature regime. The experimental results of V_2O_5 - ZrO_2 (Fig. 7) and V_2O_5 - TiO_2 (Fig. 8) expose a comparable yield of FA in both cases, since there are desirable changes of the by-product content (the rise of MA and total absence of BA and Ft).

An interesting dependence of the selectivity towards maleic anhydride is observed in the case of V_2O_5 - TiO_2 (anatase) catalysts. The experimental results in Fig. 7 show the selectivity to drop after 50 h at all space velocities. The selectivity towards *o*-xylene oxidation to CO_x shows a constant value of about 40 mol.% (Figs. 6 and 7). The kinetic tests at high temperatures ($> 440^\circ C$) show that with respect to its selectivity of *o*-xylene oxidation to phthalic anhydride and phthalide, the V_2O_5 - ZrO_2 catalyst has some advantages as compared to conventional V_2O_5 - TiO_2 (anatase) catalysts. Nevertheless, it should be noted that the selectivity of V_2O_5 - ZrO_2 catalysts in *o*-xylene oxidation to phthalic anhydride, as measured at $410^\circ C$, is by about 15% lower than that of conventional V_2O_5 - TiO_2 (anatase) catalysts (Figs. 1 and 4).

With rising temperature (up to 450 – $550^\circ C$), a V_2O_5 - TiO_2 (anatase) catalyst sample has exhibited a more pronounced decrease of selectivity in partial *o*-xylene oxidation than in the case of V_2O_5 - ZrO_2 . This decrease amounts to about 7–8 mol.% (Fig. 8), while for V_2O_5 - ZrO_2 it is 1–2 mol.% (Fig. 7).

CONCLUSION

A highly active and selective V_2O_5 - ZrO_2 -based catalyst has been synthesised. In comparison with conventional V_2O_5 - TiO_2 (a) catalyst, the V_2O_5 - ZrO_2

catalyst has shown a higher selectivity to the valuable side product maleic anhydride under conditions close to the industrial ones.

At low oxidation temperatures (up to $410^\circ C$) this catalyst is inferior to the conventional industrial V_2O_5 - TiO_2 (a) catalyst. The kinetic studies performed in a high temperature regime (above $440^\circ C$) have shown the vanadium-zirconium catalyst to surpass in properties the V_2O_5 - TiO_2 (a) catalyst under these conditions. It has been established that a high selectivity in *o*-xylene oxidation is attained when during the preparation of the V_2O_5 - ZrO_2 catalyst ZrO_2 is completely covered by VO_x .

It has been also found that a V_2O_5 - TiO_2 (a) catalyst sample containing 7 wt.% V_2O_5 demonstrates best catalytic activity expressed in highest selectivity to phthalic and maleic anhydrides and lowest selectivity to phthalide, CO and CO_2 .

In contrast to the conventional V_2O_5 - TiO_2 (a) catalyst, the V_2O_5 contents in V_2O_5 - ZrO_2 catalyst is higher than that typical for monolayer coverage.

SYMBOLS

PhA	phthalic anhydride;
Pht	phthalide;
BA	benzoic acid;
MA	maleic anhydride;
w	space velocity, h^{-1} ;
S_i	selectivity, mol.%;
C_{xylene}	concentration of <i>o</i> -xylene, g/nm^3

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V_2O_5 - ZrO_2 КАТАЛИЗАТОР ЗА СЕЛЕКТИВНО ОКИСЛЕНИЕ НА *o*-КСИЛОЛ ДО ФТАЛОВ АНХИДРИД: I. ПОЛУЧАВАНЕ, КАТАЛИТИЧНА АКТИВНОСТ И СЕЛЕКТИВНОСТ

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(Резюме)

Изследвана е термичната устойчивост, каталитичната активност и селективност на серия от V_2O_5 - ZrO_2 каталитични образци за парциално окисление на *o*-ксилол до фталов анхидрид. Каталитичната селективност на каталитичния образец със 7% V_2O_5 - ZrO_2 е сравнена с конвенционалния промишлен катализатор V_2O_5 - TiO_2 (анатаз). Термичната устойчивост е изследвана в два температурни обхвата. При ниски температури (под 410°C) V_2O_5 - TiO_2 (анатаз) показва по-ниска селективност спрямо фталов анхидрид в сравнение със синтезирания V_2O_5 - ZrO_2 каталитичен образец. При по-високи реакционни температури, дори при 550°C в продължение на 50 часа експлоатационно време, селективността спрямо целевия продукт от фталов анхидрид на V_2O_5 - ZrO_2 каталитичен образец намалява незначително.