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V_2O_5-ZrO_2 catalyst for selective oxidation of *o*-xylene to phthalic anhydride: II. Physicochemical characterisation of the catalyst

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Vanadium oxide-zirconia catalysts were prepared by impregnation of ZrO_2 powder with an aqueous solution of NH_4VO_3. The thermal stability, activity and selectivity of a series of V_2O_5-ZrO_2 catalyst samples towards *o*-xylene oxidation to phthalic anhydride have been investigated. It has been established that the phthalic anhydride content reaches about 55 mol% in samples containing 7 and 10 wt% V_2O_5. The physicochemical characterisation of the catalysts prepared was performed using IR spectroscopy, XPS analysis, X-ray spectroscopy, derivatograph analysis, EPR spectroscopy and temperature - programmed reduction.

Key words: V_2O_5-ZrO_2 catalysts, *o*-xylene oxidation, surface characterisation, physicochemical characterization.

INTRODUCTION

Vanadium oxide-based catalysts are well known and extensively employed in industry for heterogeneous oxidation and ammoxidation of aromatic hydrocarbons [1−7]. Generally these catalysts are supported on oxides such as Al_2O_3, SiO_2 and TiO_2. Supports are often found to modify the physicochemical properties of vanadia catalysts. The supported oxides do not form three-dimensional crystal phases, but rather a patchy or continuous 'monolayer' covering the support [8, 9]. Recently, ZrO_2-supported catalysts were found to exhibit better catalytic properties than the catalysts supported on other oxides [10].

During the past years some patents have reported the use of ZrO_2 as a support of V_2O_5 [11]. Systems of V_2O_5-ZrO_2 in combination with various promoters are widely used for several reactions including *o*-xylene oxidation [12], ammoxidation of aromatics and methylaromatics [13], oxidation of toluene [14, 15], decomposition of propan-2-ol [16, 17], oxidative dehydrogenation of propane [18, 19], oxidation of naphthalene [21, 23], partial oxidation of methanol and selective catalytic reduction of NO_x by C_3H_6 [20]. The utilisation of ZrO_2 is based on the fact that it is stable at very high temperatures [21] and its acid-basic characteristics are very close to those of TiO_2 .

Interesting studies [21−29] have reported the use of zirconia as a support of vanadium oxide catalysts. The valuable zirconia properties in this respect are its high thermal stability and acid-basic characteristics which are close to those of titania (anatase) [22−25].

The activity of supported vanadia catalysts depends mainly on the method of preparation, the nature of the support and the dispersion of the active component on the support surface. Considerable efforts have been made to develop surface characterisation of the active component in supported catalysts. These include specific surface area, IR spectroscopy, XPS analysis, X-ray spectroscopy, derivatograph analysis, EPR spectroscopy and temperature - programmed reduction.

EXPERIMENTAL

Synthesis 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^{5+}-V_2O_5 (specific surface area 6 m^2/g), NH_4VO_3 (AG-Fluka) and ZrO_2 (AG-Fluka; monoclinic [6], specific surface area 26 m^2/g) being used.

The catalyst samples were prepared by reducing V^{5+} of V_2O_5 (V_2O_5:$H_2C_2O_4$ = 1:2.5−3.0) in an aqueous solution of oxalic acid at 60-80°C. Zirconia was introduced simultaneously. Surfactants (formamide or diphenylformamide) in an aqueous solution: surfactants ratio = 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 of steatite spheres, 6 mm in diameter, by pulverising the suspension on

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the spheres pre-heated up to 200–250°C. The catalyst samples thus obtained had a coverage thickness of 1 mm of the total catalyst mass. 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 catalyst in air flow).

Apparatus for investigating the catalytic activity and selectivity of the samples, under study

The activity and selectivity of the catalyst samples towards the vapour phase partial oxidation of *o*-xylene to phthalic anhydride were investigated with a flow-type installation functioning at a pressure of 1 atm. The laboratory flow reactor had a length of 450 mm and contained 250 cm^3 catalysts. It was immersed in a salt bath containing a 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.

Condensers up took the vapour phase oxidation products and the gas phase was conducted to the gas chromatograph.

Methods and apparatus for characterisation of catalyst samples 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 (PhA), phthalide (Pht), benzoic acid (BA), maleic anhydride (MA) and CO_2 + CO were determined. The gas chromatograph was connected on-line with the flow installation for *o*-xylene oxidation. The catalyst samples were activated by air for 48 h, while the selectivity measurements were done 2 h after fixing the corresponding regime.

The final reaction mixture was subjected to gas-chromatographic analysis in a Perkin Elmer 850 apparatus (capillary column OV-101, 1 = 25 m, inner diameter = 0.25 mm, carrier gas = H_2, T = 90−120°C, detector PID). The reaction products found were *o*-toluyl aldehyde, benzoic acid, phthalide, maleic anhydride, phthalic anhydride and unreacted xylene. The products of fragmentary oxidation (CO and CO_2) were determined chromatographically in a steel column (l = 4 m, inner diameter = 0.25 mm, 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.

The samples were characterised by a series of physicochemical methods.

The specific surface area was measured with a Klyachko-Gurvich apparatus by the BET method.

The IR spectra were recorded by a Nicolet Avatar 320 FIIR spectrometer using KBr tablets.

The XPS analysis of V_2O_5-ZrO_2 was carried out with an Escalab II electron spectrometer at a pressure of about 10^{-8} Pa. The samples were stored in stainless steel vessels. The photoelectron spectra were excited by MgK_α radiation.

The X-ray spectra were recorded with a DRON-3 apparatus using CuK_α radiation.

The EPR spectra of the samples at room temperature were obtained by an ERS 220/Q electron resonance spectrometer system at 100 kHz modulation of the magnetic field.

Temperature-programmed reduction (TPR) was carried out on a standard laboratory apparatus using a quartz thermometer. The weight of the sample was 0.1 g. The temperature was raised linearly from 30 to 800°C at a constant heating rate of 10°/min. The samples were reduced in a 10% hydrogen + 90% argon mixture (flow-rate of 30 ml/min).

Derivatograph analysis was made with a Paulik Erdey derivatograph apparatus. This permitted simultaneous registration of the temperature curve (T), the enthalpy curve (DTA), the mass change (TG curve) and the DTG curve. The analysis was performed with a TG sensitivity of 200 mg, a sample weight of 0.5 g, a heating rate of 10°C/min, technically pure alumina as an inert substance, turbulence air in the furnace and heating up to 1000°C.

RESULTS AND DISCUSSION

In order to elucidate the behaviour of the zirconium cations in the catalyst samples, we performed the following experiment. The catalytic activity and selectivity of a 7% V_2O_5-ZrO_2 sample, 1:1 mechanic (physical) mixture of the same catalyst sample with pure ZrO_2, and a sample of pure zirconia were investigated and compared.

The experimental results in Fig. 1 show that pure zirconia oxide has very low catalytic selectivity in vapour phase oxidation of *o*-xylene to phthalic anhydride. The coordinatively unsaturated cations initiate processes of complete oxidation. On this basis it can be expected that the pure zirconia surface would lead to complete *o*-xylene oxidation. At first sight the relatively low activity of pure zirconia seems to be an indication of its inertness

towards the complete *o*-xylene oxidation to phthalic anhydride. From the scientific literature it is known that coordinatively unsaturated titanium cations also have a low activity with respect to the oxidation of *o*-xylene oxidation to phthalic anhydride. However, they favour the complete oxidation of the intermediate products of partial oxidation.

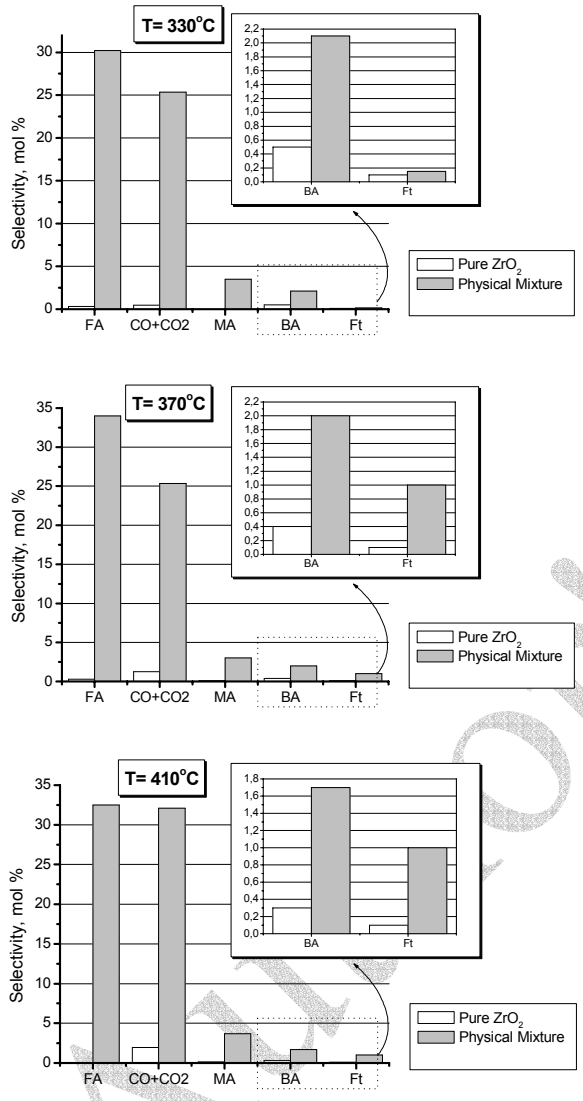

Fig. 1. Selectivity of pure ZrO_2 and a physical mixture of pure ZrO_2 and catalyst sample 7% V_2O_5-93% ZiO_2 (1:1) at a different temperature oxidation of *o*-xylene. $C_{o\text{-}xylene}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h.

Let us study the behavior of the zirconium species. If they are completely inert, a drop in catalyst activity should be observed due to the lower (50%) relative content of the active V_2O_5 phase.

The experimental results (Fig. 1) obtained at different (330, 370 and 410°C) temperatures reveal a significant drop (by about 10%) in activity of the 7% V_2O_5-ZrO_2 sample when it is mixed mechanically with pure zirconia in a 1:1 ratio. Simultaneously, the amount of CO_x in the products increases. The content of *o*-toluyl anhydride and phthalide in the oxidation products increases several times. This is also an indication of a reaction proceeding towards complete oxidation.

The experimental results permit the important, with respect to the catalyst structure, conclusion that high catalyst selectivity towards the oxidation reaction can be achieved when the zirconia surface is completely covered by VO_x. It should also be noted that the amount of the VO_x surface phase needed for monolayer coverage would not necessarily ensure the absence of a bare zirconia surface. It is known that in many cases the VO_x surface phase forms the so-called islands. A suitable method is needed for the synthesis of surface phase VO_x coverage.

Determination of specific surface

The specific surface areas are: 26 m^2/g for the initial monoclinic ZrO_2, 28 m^2/g for the obtained fresh catalyst of 7% V_2O_5-ZrO_2, 22 m^2/g for the catalyst 10 h at 450°C, and 7 m^2/g for the heated in air at 800°C for 3 h (Table 1). These data show that during the exploitation of the 7% V_2O_5-ZrO_2 catalyst at 450°C no intense sintering proceeds since the specific surface area does not change substantially. The sintering occurring at 800°C leads to a strong decrease of the specific surface area.

It should be noted that according to [30] the conventional V_2O_5-TiO_2 (anatase) catalyst is strongly sintered (deactivated) at this temperature. However, considerable sintering of the 7% V_2O_5-ZrO_2 catalyst resulting in a specific surface area drop has been observed at 800°C.

Derivatograph analysis (DTA, DTG, TG)

The DTA curve of the synthesised catalyst sample (7% V_2O_5-93% ZrO_2) exhibits a double exothermic effect beginning above 100°C and showing a maximum at about 260°C, then a second maximum at 365°C. The latter is visible within the same temperature range on the TG curve (Fig. 2) and is produced by a two-stage decomposition process. According to our opinion this may be due to further decomposition of the vanadium-oxalate complex used as a precursor in preparation of catalysts samples. The supposition is confirmed by IR and X-ray phase analyses of the catalyst samples. The total weight drop of the sample indicates about 93% of undecomposed oxalate complex.

The DTA curve (Fig. 3) of the same catalyst sample (7% V_2O_5-93% ZrO_2) after 100 h exploitation in *o*-xylene oxidation to phthalic anhydride at 450°C displays one barely visible exothermic effect at 230−290°C with a maximum at 260°C. It is

probably a result of additional decomposition, which is indicated by the DTG and TG curves within the same temperature range.

XP spectroscopy

The XPS studies of the catalyst samples have registered Ti $2p^{3/2}$ and Zr $3d^{3/2}$ lines. On the surface there are only ZrO_2 and TiO_2 in the 4^+ oxidation state. This is evident from Figs. 4 and 5 presenting the XPS spectra of Ti2*p* and Zr3*d*. The chemical shift of the above lines is characteristic of TiO_2 and ZrO_2. In both substrates (Figs. 4 and 5) vanadium is in the same oxidation state as V_2O_5, which is proved by the shift of the V $2p^{3/2}$ lines.

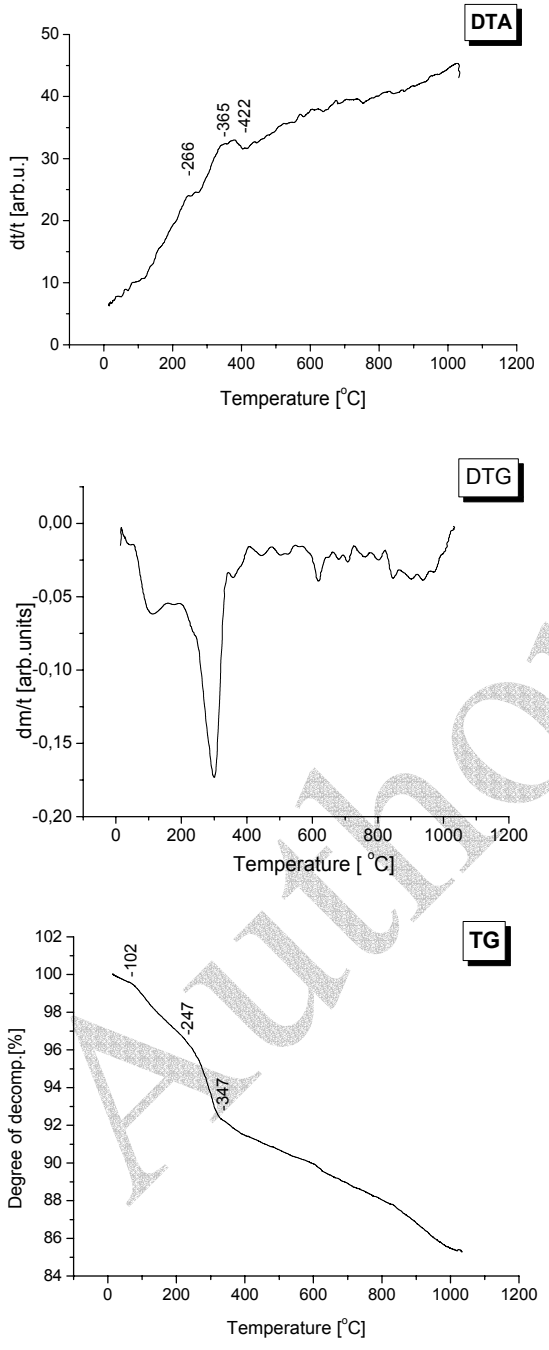

Fig.2. Derivatograph analysis (DTA, DTG, TG) of fresh 7% V_2O_5-93% ZiO_2 catalyst sample.

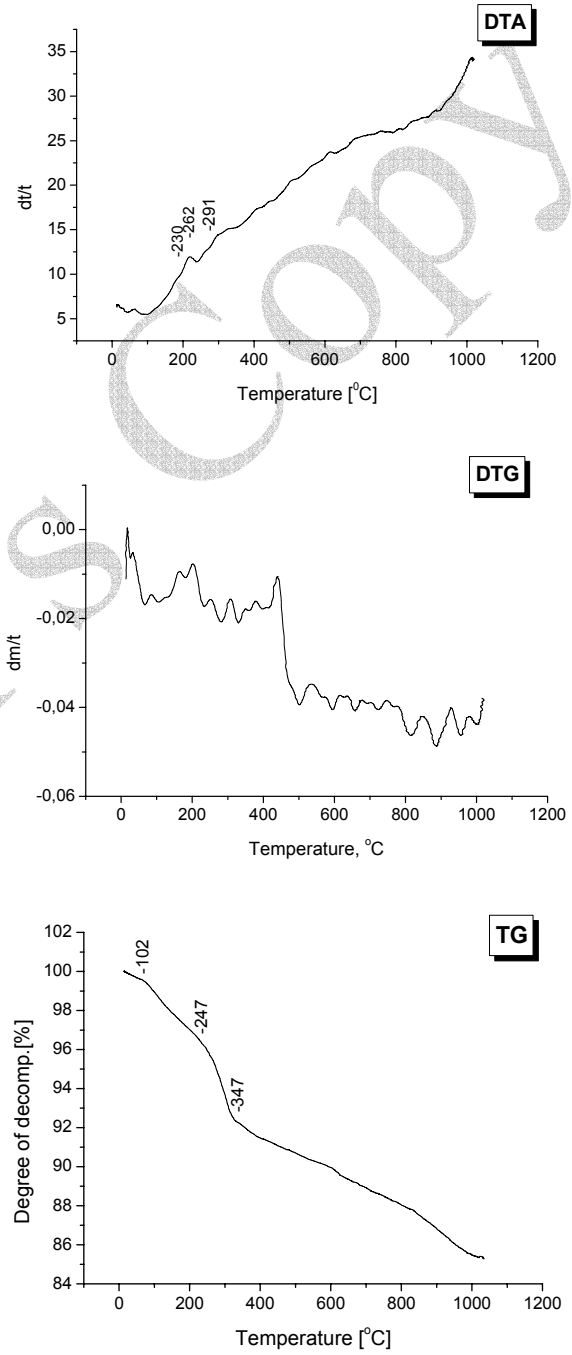

Fig. 3. Derivatograph analysis (DTA, DTG, TG) of catalysts samples 7% V_2O_5-93% ZiO_2 tested in *o*-xylene oxidation, T=370°C, $C_{o\text{-}xylene}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h.

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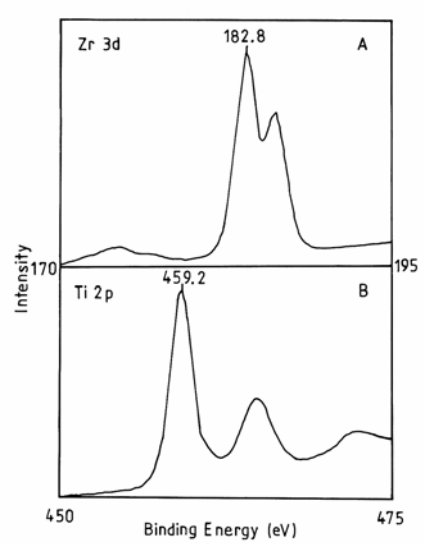

Fig. 4. Photoelectron spectra of pure ZrO_2 (curve A) and pure TiO_2 (anatase) (curve B).

The Ti:V:O or Zr:V:O concentration ratio (at.%) calculated on the basis of XPS experiments (Table 1) is, after correcting the free path of photoemitted electrons, in a very good agreement with the above considerations.

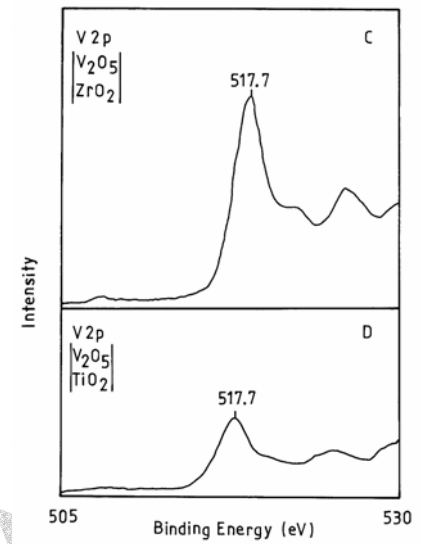

Fig. 5. Photoelectron spectra of catalyst sample 7% V_2O_5-93% ZiO_2 (curve C) and catalyst sample 7% V_2O_5-93% TiO_2 (anatase) (curve D), tested in *o*-xylene oxidation (curve B), T = 370°C, $C_{o\text{-xylene}}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h.

Thermoprogrammed reduction

The catalyst samples were subjected to temperature programmed reduction. Figures 6 and 7 present results from TPR of fresh V_2O_5-ZrO_2 samples containing different V_2O_5 concentrations (from 4 to about 10%). The peaks observed up to 300°C with samples a, b and c are probably due to desorption of water from the samples. Two more groups of peaks are observed: low-temperature peaks at 340−360°C and high-temperature ones at 460−480°C. According to literature [49, 50], the low-temperature peaks are characteristic of the reduction of V_2O_5 crystals, while the high-temperature ones are produced by reduction of surface vanadium. The areas of the low-temperature peaks (a-c) show an obvious trend to increase with the V_2O_5 content. The same trend, although much less pronounced, is observed with the areas of the high-temperature peaks.

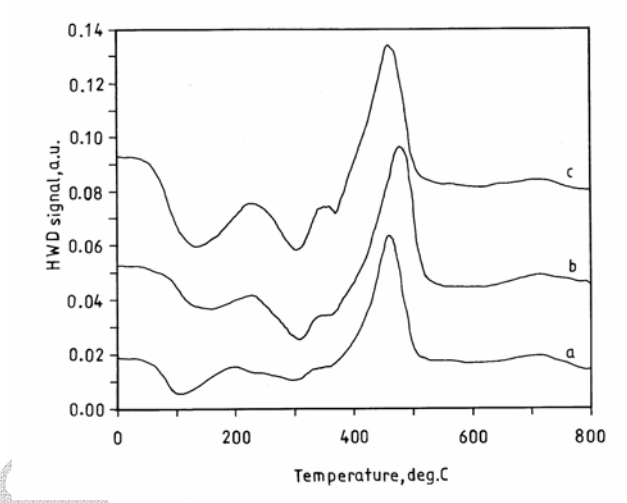

Fig. 6. Temperature-programmed reduction of fresh catalysts systems V_2O_5-ZiO_2 at different contents of V_2O_5 (wt.%): a. catalyst sample 4% V_2O_5-96% ZiO_2; b. catalyst sample 7% V_2O_5-93% ZiO_2; c. catalyst sample 10% V_2O_5-90% ZiO_2.

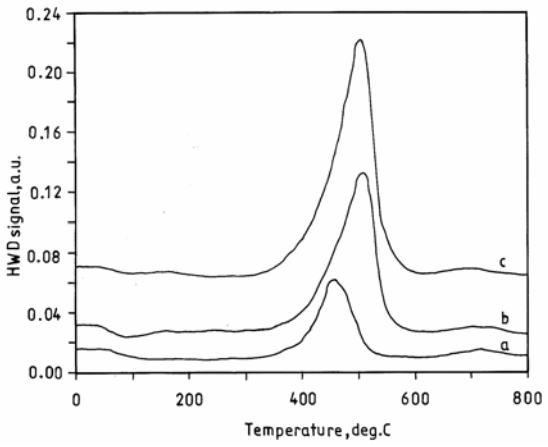

Fig. 7. Temperature-programmed reduction of tested in *o*-xylene oxidation catalysts systems V_2O_5-ZiO_2, T = 450°C, $C_{o\text{-xylene}}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h at different contents of V_2O_5 (wt.%): a. catalyst sample 4% V_2O_5-96% ZiO_2; b. catalyst sample 7% V_2O_5-93% ZiO_2; c. catalyst sample 10% V_2O_5-90% ZiO_2.

Comparison of the data from TPR of a conventional V_2O_5-TiO_2 (anatase) catalyst [31, 32] with those on V_2O_5-ZrO_2 shows a low-temperature peak

much smaller than the high-temperature one in the first case. This is attributed to the fact that the V_2O_5-TiO_2 (anatase) catalyst samples contain a much larger amount of surface vanadium. On the zirconia substrate, vanadium is coordinated much more easily and is more difficult to remove than in the case of the titania (anatase) support. Taking into account that V_2O_5 is the active phase, the V_2O_5-ZrO_2 catalyst should have a good catalytic activity.

The spectra of used in process of oxidation of *o*-xylene V_2O_5-ZrO_2 catalyst samples (Fig.7) show a single peak at 450−510°C, which is probably due to the reduction of surface vanadium. With increasing V_2O_5 amount in samples a-c, the peak areas increase. The ratio between the areas of the peaks for fresh and used samples also increases with the active phase (V_2O_5) concentration in the direction a-c.

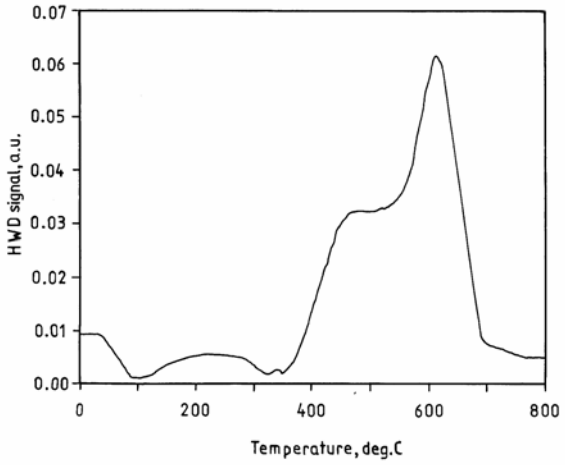

Fig. 8. Temperature-programmed reduction of tested in *o*-xylene oxidation catalysts sample 7% V_2O_5-93% TiO_2 (anatase), T = 450°C, $C_{o\text{-}xylene}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h.

For the sake of comparison, a 7% V_2O_5-TiO_2 (anatase) sample was also subjected to TPR. Figure 8 shows the spectrum, which is very close to that of the conventional V_2O_5-TiO_2 (anatase), described in literature [30]. The low-temperature peak is observed at about 460°C. It is due to reduction of surface vanadium. A high-temperature peak, much more intense than the low-temperature one, is observed at 600°C. No such peak has been established with V_2O_5-ZrO_2 samples. According to Wachs *et al.* [30], this peak is due to the partial reduction of V_2O_5 probably to V_2O_4 during the catalytic reaction. A low-intensity peak is observed at 340−350°C. Its presence indicates that not completely reduced crystallites of V_2O_5 have remained in the used catalyst sample.

Previous studies on the catalytic activity of the V_2O_5-ZrO_2 system [33] have shown values commensurable with those for the system V_2O_5-TiO_2. Taking into account this and the experimental results of TPR one may draw some conclusions on the role of the V_2O_5 active phase with respect to the catalytic properties of the samples.

The relatively high catalytic activity of samples of the V_2O_5-ZrO_2 system may be due to distribution of the active sites on the surface of the vanadium support. This assumption is based on the fact that the peak area of 7% V_2O_5-ZrO_2 – used in oxidation of *o*-xylene (Fig. 7) is much larger that the area of the low-temperature peak in the spectrum of using V_2O_5-TiO_2 (anatase) sample (Fig. 8).

The high catalytic activity of the catalyst sample from the V_2O_5-TiO_2 (anatase) system shows that the partial reduction of V_2O_5 to V_2O_4 is also of importance for the catalytic reaction.

EPR spectroscopy

Figure 9 shows the EPR spectra of fresh V_2O_5-ZrO_2 catalyst samples as well as of samples used in *o*-xylene oxidation to phthalic anhydride.

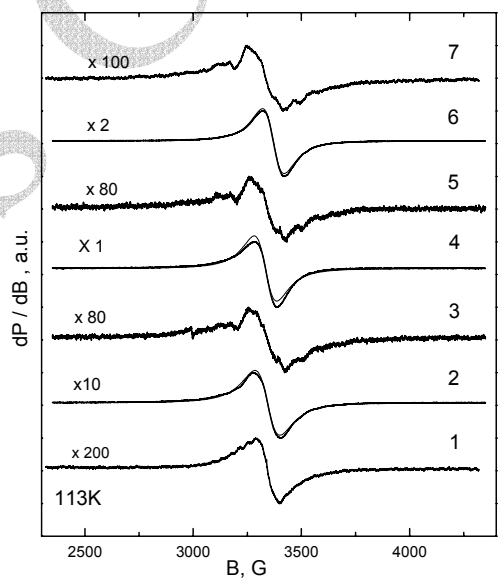

Fig. 9. EPR spectra of the catalyst system V_2O_5-ZiO_2: 1. pure V_2O_5; 2. fresh catalyst sample 4% V_2O_5-96% ZiO_2; 3. tested in *o*-xylene oxidation catalyst 4% V_2O_5-96% ZiO_2, T = 450°C, $C_{o\text{-}xylene}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h; 4. fresh catalyst sample 7% V_2O_5-93% ZiO_2; 5. tested in *o*-xylene oxidation catalyst 7% V_2O_5-93% ZiO_2, T = 450°C, $C_{o\text{-}xylene}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h; 6. fresh catalyst sample 10% V_2O_5-90% ZiO_2; 7. tested in *o*-xylene oxidation catalyst 10% V_2O_5-90% ZiO_2, T = 450°C, $C_{o\text{-}xylene}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h.

In the same figure a comparison with the EPR spectrum of a sample of V_2O_5 is made. Evidently, the EPR spectrum of V_2O_5 (curve 1) consists of a single line on which an unresolved fine structure is

visible. According to the data from literature [34, 35], this signal may be ascribed to exchange-associated VO^{2+}complexes. The spectra (2, 4 and 6) of fresh catalyst samples exhibit a single line with a Lorentzian shape whose width slightly decreases with increasing the amount of supported V_2O_5 (from curve 2 to curve 6): curve 2: 4% V_2O_5-96% ZrO_2 – ΔH_{pp} = 115 ± 1G; curve 4: 7% V_2O_5-93% ZrO_2 – ΔH_{pp} = 104 ± 1G; curve 6: 10% V_2O_5-90% ZrO_2 – ΔH_{pp} = 100 ± 1G.

The model V_2O_5 used as a standard has about 200 times lower intensity as compared to the EPR signal of the sample where V_2O_5 is the active phase.

With the catalyst samples used in *o*-xylene oxidation to phthalic anhydride (Fig.9, curves 3, 5 and 7), the intensity of the EPR signal sharply drops and the EPR spectra (Fig. 9, curves 3, 5 and 7) contain an asymmetric signal of isolated VO^{2+} complex group.

In these catalyst samples the amount of exchange-associated VO^{2+} groups decreases. The appearance of isolated VO^{2+} groups (having not changed during the catalytic reaction) can be attributed to that part of the active V_2O_5 phase, which has partly interacted with zirconia support.

The period of exploitation of catalyst depends significantly on their thermal stability. The EPR spectra of a fresh 7% V_2O_5-ZrO_2 catalyst and catalysts samples calcined at 450°C and 800°C for 10 h are show in Fig. 10.

The EPR spectrum of a fresh 7% V_2O_5-ZrO_2 catalyst (Fig. 10, curves 1a–1c) shows two signals: a singlet signal being 11 mT wide (curve 1a) and an octet signal, which is not well solved (curve 1b). The combination of both signals (curve 1a and 1b) leads to the registration of a total signal presented in Fig. 5 by a thick line (curve 1c). According to the authors [34, 36], these two signals are due to clustering V^{4+} (with respect to the singlet signal) and to a VO^{2+} complex (for the octet signal).

The form and the view of EPR spectrum of a catalyst sample calcined at 450°C for 10 h (curve 2a–2b) do not differ practically from that of a fresh catalyst (Fig. 10, curves 1a–1c). This means that there is no significant change of the fine structure of the active phase (V_2O_5) of the catalyst calcined at 450°C. The thermal treating of the catalyst under this temperature has practically no influence on its thermal stability. On the contrary, a V_2O_5-TiO_2 (anatase) catalyst undergoes consider-able structural changes under such conditions of calcination.

An appreciable variation of the shape of the EPR spectrum of a sample calcined at 800°C for 10 h is observed (Fig. 10, curve 3). The singlet signal (clustering V^{4+}) disappears and is completely compensated by the octet signal due to the VO^{2+} complex. The last one is presented in Fig.10 by a thick line (curve 3).

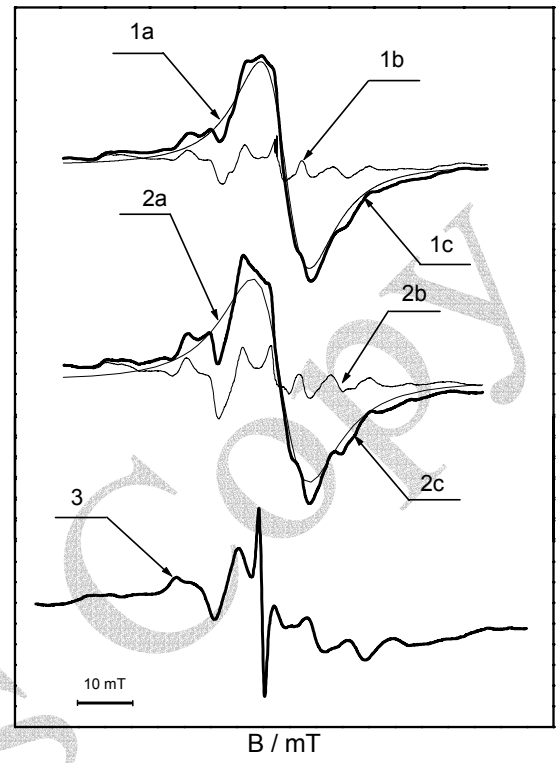

Fig. 10. EPR spectra of 7% V_2O_5-93% ZiO_2 catalyst sample. curves 1a-1c – fresh catalyst; curves 2a-2c – catalyst calcined at 450°C for 10h; curves 3a-3c – catalyst calcined at 800°C for 10h

X-ray phase analysis

The X-ray phase analysis of catalyst samples used in the *o*-xylene oxidation to phthalic anhydride shows the presence of a crystalline phase of mono-clinic zirconia with all catalysis samples (Fig. 11). Peaks of the supported V_2O_5 phase are not visible, which indicates that at the working temperature of the catalyst samples (450°C) it is amorphous or clusters of V_2O_5 particles have been formed. Well shaped V_2O_5 crystals have not been observed.

The intensity of the zirconia peaks decreases with the increase in V_2O_5 concentration (from 3 to 1 in Fig. 11). The mean thickness of the V_2O_5 coverage in the whole bulk surface of the zirconia support was estimated from the decrease in integral intensities of the zirconia peaks due to absorption of the X-rays by the catalyst layer.

The calculations were performed according to the formula [37]:

$$I = I_0 e^{\frac{-\mu}{\rho}\rho\frac{2t}{\sin\theta}}$$

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$$\frac{\mu}{\rho} = \frac{1}{M}\sum\left(\frac{\mu}{\rho}\right)_i m_i$$

$$t = -\frac{1}{2}\ln\frac{I}{I_0}\sin\frac{\Theta}{\mu},$$

where I denotes the integral intensity of the of 7% V_2O_5-93% ZrO_2 sample, Io − the integral intensity of the peak of zirconia, μ − absorption coefficient, ρ − the density (g·cm3), t − the density of the coverage and θ is the angle for which the intensities I and Io are calculated. According to the calculations, the mean thickness of the V_2O_5 coverage in the whole bulk surface of the zirconia support of the 7% V_2O_5-93% ZrO_2 catalyst is 375 nm.

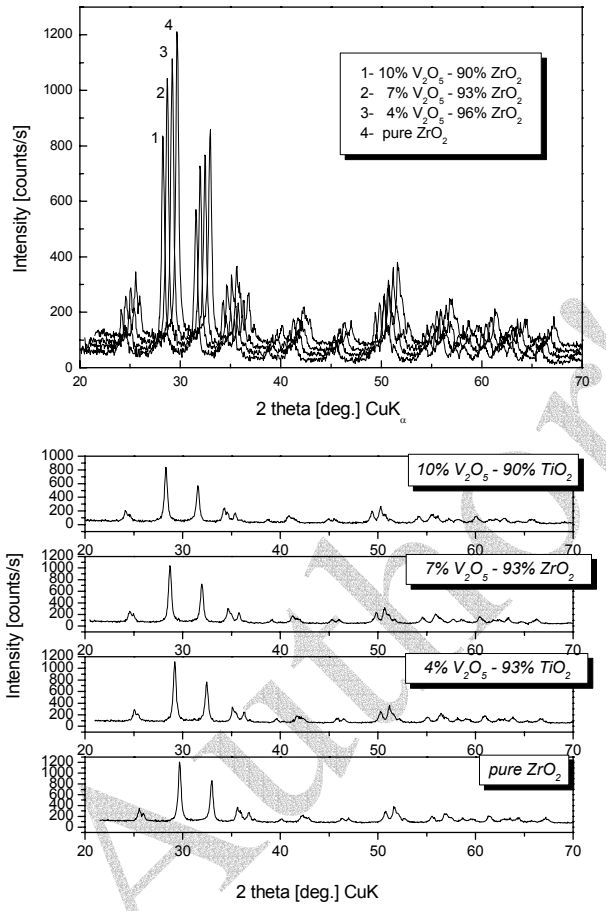

Fig. 11. X-ray spectra of the catalyst system V_2O_5-ZiO_2: 1. tested in *o*-xylene oxidation catalyst 10% V_2O_5-90% ZiO_2, T = 450°C, $C_{o\text{-xylene}}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h; 2. tested in *o*-xylene oxidation catalyst 7% V_2O_5-93% ZiO_2, T = 450°C, $C_{o\text{-xylene}}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h; 3. tested in *o*-xylene oxidation catalyst 4% V_2O_5-96% ZiO_2, T = 450°C, $C_{o\text{-xylene}}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h; 4. pure ZrO_2.

IR Spectroscopy

Figure 12 shows the IR spectra of the fresh synthesised sample (with 4 and 7% V_2O_5) and catalysts samples tested in *o*-xylene oxidation.

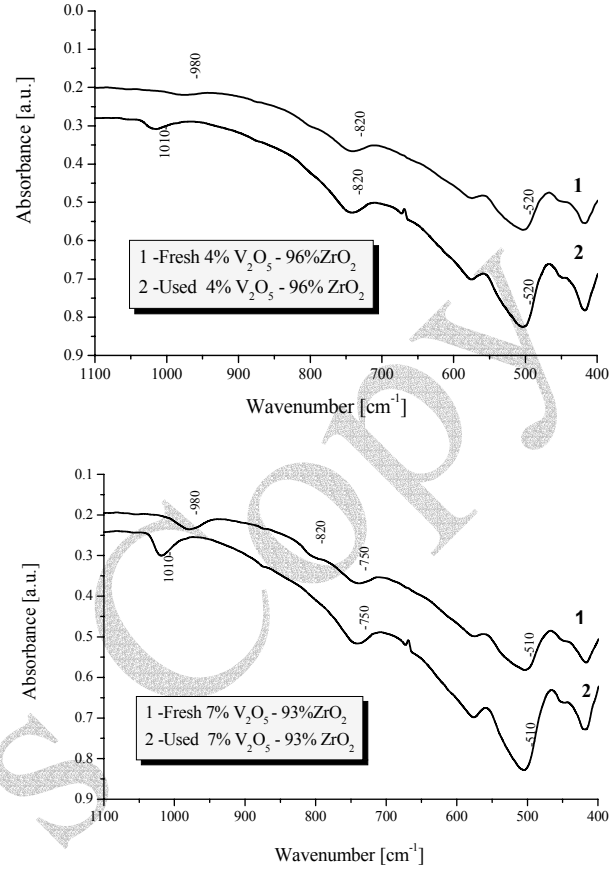

Fig. 12. IR spectra of catalysts samples 4% V_2O_5-96% ZiO_2 and 7% V_2O_5-93% ZiO_2: 1 - fresh catalysts samples; 2 - tested in *o*-xylene oxidation catalysts samples, T = 450°C, $C_{o\text{-xylene}}$ = 42 g/nm^3, w = 1500 h^{-1}, time of exploitation τ = 10 h.

The IR spectra of use catalyst samples contain absorption bands at 1010, 820 and 520 cm^{-1}, which are characteristic of pure V_2O_5. The high-frequency band at 1010 cm^{-1} is assigned to vibration of isolated V=O non-bridge bonds in the [VO_5] trigonal bipyramids [38, 39]. The broad absorption band at 810 cm^{-1} is due to stretching modes of V–O–V chains, while the bands at 500 and 430 cm^{-1} are associated with bending modes of the V_2O_5 network consisting of [VO_5]. The intensity of these absorption bands is higher than that of the band of fresh catalyst samples. This may be a result of crystallisation processes initiated by the temperature of *o*-xylene oxidation.

A characteristic feature of the IR spectra of fresh catalyst samples is the shift of the absorption lines of [VO_5] groups to lower frequencies, which is probably due to lengthening of the V–O bonds.

The IR spectra of 7% V_2O_5-93% ZrO_2 system treated at 450 and 800°C (normalised with respect to the most intensive peak at 501 cm^{-1}) are presented

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in Fig. 13. The spectra of both samples (curve 1 - 450°C and curve 2 - 800°C) in the region of 1100−400 cm^{-1} do not show significant variations in the structure of the active phase. The reason for such a statement is the fact that the positions of the peaks (characteristic for the system V_2O_5-ZrO_2) of the absorption band coincide. On the other side, it can be seen that the intensity of the peak at 1020 cm^{-1} for the catalyst sample calcined under 800°C (curve 2) increases significantly. Most probably this is due to crystallisation processes taking place at this high temperature. In our point of view, they lead to an intensive sintering of the catalyst sample and as a result the adsorption characteristics of the support decline and the thermal stability of the catalyst being worsened, respectively. This is in accordance with the specific surface data (Table 1). It is worth noting that in the interval 450−800°C a separation of the water occurs and the peak observed at 1633 cm^{-1} for a sample calcined at 450°C (curve 1) disappears (curve 2) (deformation fluctuation of the water). The peaks observed in the spectrogram 1 at 1384 and 1458 cm^{-1} are very likely due to the thermal decomposition of the binding agent that is used in the synthesis of the catalyst.

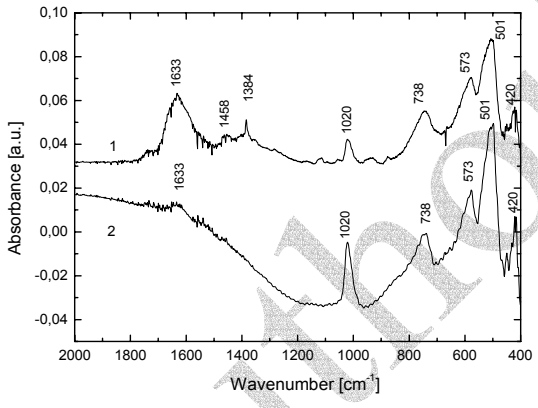

Fig. 13. IR spectra of 7% V_2O_5-93% ZiO_2 catalyst sample: 1 - catalyst samples calcined at 450°C for 10 h; 2 - catalyst samples calcined at 800°C for 10 h.

CONCLUSIONS

The physicochemical characterisation of prepared V_2O_5-ZrO_2 catalyst samples was performed using IR spectroscopy, XPS analysis, X-ray spectroscopy, derivatograph analysis, EPR spectroscopy and temperature-programmed reduction.

A high catalyst selectivity towards the oxidation reaction can be achieved when the zirconia surface is completely covered by VO_x. The amount of the VO_x surface phase needed for monolayer coverage would not necessarily ensure the absence of a bare zirconia surface.

In the synthesised V_2O_5-ZrO_2 and V_2O_5-TiO_2 catalyst samples vanadium is in the same oxidation state as V_2O_5, which is proved by the shift of the V $2p^{3/2}$ lines.

The relatively high catalytic activity of samples of the V_2O_5-ZrO_2 system may be due to distribution of the active sites on the surface of the vanadium support. The high catalytic activity of the catalyst sample on the base of V_2O_5-TiO_2 (anatase) system shows that the partial reduction of V_2O_5 to V_2O_4 is also of importance for the catalytic reaction.

The EPR analyses of fresh V_2O_5-ZrO_2 catalyst samples expose the presence of exchange-associated VO^{2+} complexes and isolated VO^{2+} complex groups. The appearance of isolated VO^{2+} groups (having not changed during the catalytic reaction) can be attributed to that part of the active V_2O_5 phase which has partly interacted with zirconia support.

The thermal treating of the catalyst has practically no influence on its thermal stability. On the contrary, a V_2O_5-TiO_2 (anatase) catalyst undergoes considerable structural changes under such conditions of calcinations.

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V_2O_5-ZrO_2 КАТАЛИЗАТОР ЗА СЕЛЕКТИВНО ОКИСЛЕНИЕ НА *о*-КСИЛОЛ ДО ФТАЛОВ АНХИДРИД: II. ФИЗИКОХИМИЧНО ОХАРАКТЕРИЗИРАНЕ

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(Резюме)

V_2O_5-ZrO_2 катализатор е синтезиран чрез нанасяне на прах от ZrO_2 с воден разтвор NH_4VO_3. Изследвана е термичната устойчивост, каталитичната активност и селективност на серия от V_2O_5-ZrO_2 катализаторни образци спрямо окислението на *о*-ксилол до фталов анхидрид. Установена е селективност около 55 мол.% за образци съдържащи 7 и 10% V_2O_5. Направена е физикохимична характеристика на катализаторните образци с помощта на инфрачервена спектроскопия, рентгенофазов анализ, ЕПР анализ, деритографски анализ и термопрограмирана редукция.