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CHARACTERIZATION OF V-BASED SUPPORTED CATALYSTS FOR OXIDATIVE DEHYDROGENATION OF PROPANE AND PARTIAL OXIDATION OF CROTONALDEHYDE

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The vanadium oxide supported catalysts (1 wt. % of vanadium on SiO_2– (silica, aerosil), TiO_2– anatase, ZrO_2, Al_2O_3 – γ-alumina, MgO) were prepared by impregnation method and characterized by means of XRF, N_2-BET, H_2-TPR methods. By means of H_2-TPR, four different VOx units were determined on the catalyst surface – monomer VOx, oligomer VOx units, bulk V_2O_5 and inter-oxide species for the basic supports. The catalytic activity of these catalysts was tested in two different oxidation reactions: oxidative dehydrogenation of propane and partial oxidation of crotonaldehyde (but-2-enal) in gas phase. The catalyst prepared were active in both studied reactions, but the activity of the catalyst in each reaction was attributed to different catalytic active sites. The reaction rate of both reactions is in correlation with the given types of active sites: monomer

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VOx exhibited activity in C_3H_8 oxidative dehydrogenation, on the other hand oligomer units of VOx were active in partial oxidation of crotonaldehyde. Using of the most acid catalysts resulted in high selectivity in oxidative dehydrogenation reactions. Moreover, reaction scheme for crotonaldehyde oxidation was suggested where the formation of furan proceeds via the oxidative dehydrogenation of cis-crotonaldehyde isomerized on an acid site of the catalyst, followed by the possible subsequent oxidation of furan to maleic anhydride (furan-(2,5)-dione). The partial oxidation of crotonaldehyde via crotonic acid (but-2-enoic acid) is the second parallel pathway of the formation of maleic anhydride.

Introduction

Utilization of abundant and cheap hydrocarbons in their transformation to more economically favourable compounds is one of important challenges in the heterogeneous catalysis. Alkanes are among ones of the most available raw materials, nowadays rarely used for chemical purposes [1]. There exists a problem of the high stability of alkanes and therefore their low reactivity, hence it is necessary to use a very active catalytic system. The catalysts based on VOx are frequently used for oxidation reactions of organic compounds due to their easy activation of C-H bond on surface of this catalytic system. It is possible to give some examples of a successful use of this catalytic system *e.g.* the partial oxidation of butane, benzene, xylene, selective reduction of NOx [2,3].

The catalysts based on vanadium oxide are not generally used in its bulk form but frequently as VOx supported on various supports. The supports are utilized to modify at least mechanical properties (e.g. thermostability, surface area) of catalysts, but very often both the redox and acid-base behaviour of the catalyst is affected by the supports too [4]. The correct choice of support and method of preparation can dramatically affect the catalytic activity and selectivity of the catalyst prepared. One of the mostly used methods of preparation of supported catalysts is the impregnation of the support oxide by a source solution. Although this method of preparation of catalysts is very simple, it is rather nonspecific and prepared samples of catalysts can contain vanadium oxide in various forms, therefore preparation conditions must be controlled well and catalysts must be characterized carefully [2].

Vanadium oxide can occur on the surface in several forms as a bulk oxide or dispersed into units with single vanadium atoms bonded to the surface *via* bridging oxygen atoms. An intermediate between the mentioned extremes are the so-called oligomer species of several VOx units bonded to the surface [2, 5]. The arrangement of oxygen atoms surrounding the vanadium atom is crucial for the catalytic behaviour. It is possible to distinguish three different types of oxygen: (i) oxygen atoms bonding vanadium to the surface of the support that are, as commonly accepted, nearly inactive, (ii) oxygen atoms double-bonded to one vanadium atom, (iii) oxygen atoms bridging two vanadium atoms in oligomeric species and bulk oxides [3, 5].

The VOx based catalysts supported on various supports are active in oxidation reactions of organic compounds. The studies of the activity of these systems (VOx on SiO_2 (silica, aerosil), TiO_2 – anatase, ZrO_2, Al_2O_3 – γ–alumina, MgO) in two different reactions are the subject of this article. The first reaction was the oxidative dehydrogenation of propane to propene, the second reaction was the partial oxidation of crotonaldehyde (CA) to furan (FU) and maleic anhydride (MA). According to Kung [6], it is generally accepted that the reaction can proceed *via* two different mechanisms: the oxidative dehydrogenation (formation of propene and furan) proceeds by the β-elimination, and maleic anhydride is formed by the alkoxy mechanism. The main difference between these reactions is assumed to be the number of oxygen atoms consumed in one elementary step. The oxidative dehydrogenation reaction consumes one oxygen atom for the formation of propene or furan, whereas the alkoxy mechanism of the MA formation requires four oxygen atoms. The Mars–van Krevelen mechanism [7] is generally accepted as a suitable formal description of such catalytic reactions. The catalytic reaction (*i.e.* reaction of organic compound) on catalytic site in oxidized state is followed by reoxidation of the active site by molecular oxygen in this mechanism.

Experimental

Preparation of Catalysts

A set of catalysts containing 1 wt. % of vanadium on supports (SiO_2 – silica, aerosil, TiO_2 – anatase, ZrO_2, MgO (all chemicals of at least 99% purity from Sigma Aldrich) and Al_2O_3 – γ-alumina (Alfa Aesar – puriss)) were prepared by impregnation of NH_4VO_3 (Sigma Aldrich p.a.) on supports by the method described below. The water solution of NH_4VO_3 was prepared and mixed with various supports. The volume of the mixture was adjusted to 200 ml by addition of ethanol. The mixture was stirred at 60 °C for 1.5 hour and evaporated to dryness. The precursors were dried at 120 °C for 2 hours and then calcined at 300 °C for 12 hours.

Characterization of Catalysts

The content of vanadium in the catalyst was determined by means of XRF [8] or by means of ICP-OES in the case of VOx-TiO_2 catalyst. The specific surface of supports and samples of catalysts was determined by the N_2-BET method at 77 K using the chromatographic method [9].

The redox behaviour of VOx species on individual supports and bulk oxide (V_2O_5 — prepared by thermal decomposition of NH_4VO_3) was tested by means of hydrogen temperature programmed reduction (H_2-TPR). A 75 mg sample in a quartz U-tube microreactor was oxidized in oxygen flow at 500 °C (2 hours). The reduction proceeds from room temperature to 800 °C with a temperature gradient of 10 °C min^{-1} in a stream of hydrogen (5 vol. % H_2 in Ar). The changes of hydrogen concentration were monitored on TCD detector (Labio). The catalyst VOx-SiO_2-silica was also reduced by CO (5 vol. % of CO in He). The condition was same as for H_2-TPR experiment and quadrupole mass spectrometer OmniStar™ GDS 300 (Pfeiffer, Germany) was used for detection of changes in effluent gases. Mass fractions of 2, 18, 28, 32 and 44 were monitored simultaneously. The intensities of the individual mass fractions were recorded every 3 s in all tests.

Catalytic Tests

The propane oxidative dehydrogenation (C_3-ODH) reaction runs were carried out using a plug-flow fixed-bed reactor at atmospheric pressure at steady state conditions. Typically, 1 g of catalyst (0.25-0.5 mm) was mixed with 2 ml of inert silicon carbide (total volume of catalytic bed 2 cm^3) to avoid overheating of the catalytic bed. The catalysts were usually pre-treated with a flow of oxygen at 450 °C for 2 hours before each reaction run. The feed composition was $C_3H_8/O_2/He = 5/2.5/92.5$ vol. % — with a total flow rate of 6 $dm^3\ hr^{-1}$. The catalytic activity was compared at 450 °C and at the same time-on-stream (TOS = 200 min). The composition of the reaction products was analyzed by an on-line connected gas-chromatograph (GC – CHROM-5) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). The products of propane oxidative dehydrogenation were separated on a packed column (Porapak Q + Porapak S 1:1), molecular sieve was used for the separation of permanent gases.

The catalytic test of partial oxidation of crotonaldehyde (CA) was carried out in a through-flow apparatus with fixed-bed tube reactor at the atmospheric pressure in temperature range from 260 to 420 °C by step-by-step increasing. The reaction mixture consisted of 2 vol. % crotonaldehyde, of 4 vol. % oxygen and the rest of nitrogen. This composition of the reaction mixture was chosen according to the stoichiometry of the oxidation of crotonaldehyde to maleic anhydride. The requested concentration of crotonaldehyde in the reaction mixture was obtained by passing of a part of the nitrogen stream through a saturator kept at constant temperature. The total flow rate was constant 5 $dm^3\ hr^{-1}$. The catalytic test was carried out using 0.4 g catalyst (grains 0.25 – 0.5 mm) diluted with SiC (the total volume of catalytic bed was 5 cm^3) to avoid overheating of the catalytic bed. The products were analysed by gas chromatograph CHROM 5 equipped with a TCD detector, connected on-line to the catalytic apparatus. The organic compounds were separated using a 2.5 m packed column with 5 % Carbowax on Carboblack (Restek). Carbon dioxide was analysed using a 2.5 m Silica gel packed column (Supelco). Oxygen and carbon monoxide were separated on a 3.5 m 13X Molecular Sieve packed column (Supelco).

Results

Characterisation of Catalysts

The vanadium content was determined by means of XRF and ICP-OES techniques. Although the theoretical concentration of vanadium after the impregnation was 1 wt. %, the real vanadium content in the catalysts was decreased (Table I) by sticking of V_2O_5 on the wall of the vessel during the preparation. Vanadium losses during calcination were not expected, because the temperature of 300 °C is not sufficient for sublimation of the bonded vanadium compounds (V_2O_5 Tamman temperature is 370 °C) [2].

The specific surface area (see Table I) was measured on the basis of the N_2 adsorption isotherm and calculated from the Brunauer–Emmet–Teller equation (N_2-BET) [10]. No significant changes of surface area were detected after the impregnation process. The only exception was observed in the case of the VOx-MgO catalyst, whose specific surface decreases after the impregnation due to the formation of inter-oxide compounds mentioned by Mamedov and Cortrés Corberán [11]. The vanadium species surface density was

Table I Characterisation of VOx catalysts on various supports; vanadium content, specific surface area of support (SSA_{sup}) and catalyst (SSA_{cat}), characteristics of H_2-TPR reduction profile and acid-base character of support (IEP) [12]

Support	V content, wt. %	SSA_{sup}, $m^2\,g^{-1}$	SSA_{cat} $m^2\,g^{-1}$	density[a], VOx nm^{-2}	T_{onset}, °C	T_{max1} °C	T_{max2}, °C	L_2/L_{total}[b]	IEP [12]
SiO_2 – silica	0.73	188	204	0.04	467	568	660	0.387	2
SiO_2 – aerosil	0.99	256	262	0.04	478	570	670	0.397	1
TiO_2 – anatase	0.91	9	9	1.22	438	541	686	0.062	6
Al_2O_3 – γ alumina	0.93	102	111	0.10	413	547	738	0.174	8
ZrO_2	0.67	5	4	2.04	391	546	762	0.004	6.7
MgO	0.80	80	55	0.17	347	571	nd	nd	12.4
SiO_2- silica[c]	0.73	188	204	0.04	465	571	680	0.156	2
SiO_2- silica[d]	1.12	188	181	0.08	463	570	665	0.450	2

nd not detected

[a] number of vanadium atoms per square nanometer

[b] area ratio of high-temperature peak (oligomeric units) to total area of H_2-TPR profile

[c] VOx – SiO_2 – silica catalyst after pretreatment in CO (5 vol.% for 2 hrs. at 800 °C)

[d] VOx – SiO_2 – silica catalyst with higher V content (1.12 wt. %)

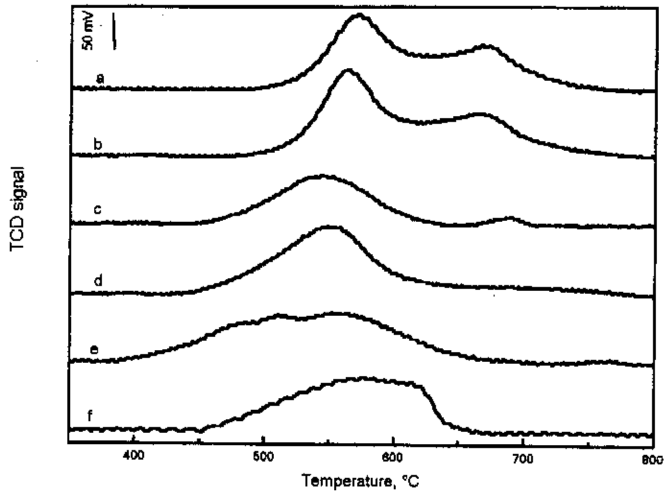


Fig. 1 The H_2-TPR spectra of VOx catalysts on various supports. a) VOx-SiO_2 (silica); b) VOx-SiO_2 (aerosil); c) VOx-TiO_2 – anatase; d) VOx-ZrO_2; e) VOx-Al_2O_3 – γ-alumina, f) VOx-MgO.

calculated from the specific surface area and vanadium content. The calculated values were below monolayer capacity mentioned by Wachs and Weckhuysen [5], which is eight VOx units per square nanometer for all used supports except SiO_2, whose monolayer capacity published in Ref. [5] is 0.7 VOx nm^{-2}. The low values of surface density of investigated catalysts allow the dispersion of vanadium on the surface and hinders the formation of bulk oxide.

The redox properties of VOx units on different supports were investigated by means of temperature programmed reduction by hydrogen (H_2-TPR). The reduction pattern exhibits two peaks (Fig. 1) and their relative intensities differ. The maxima and relative areas of peaks are given in Table I. The temperature of the maximum of the low-temperature peak (T_{max1}) was almost constant (550 – 570 °C), although the high-temperature peak (T_{max2}) exhibits dramatic changes in temperature as well as in intensity. The high-temperature peak is the most intensive in the case of SiO_2 support. Decrease in intensity of high-temperature peak is accompanied by shifting of temperature maxima to higher values with individual supports from 660 to 760 °C for VOx-SiO_2 and VOx-ZrO_2. An exception was found in the case of VOx-MgO, because of the change of the redox behaviour of the inter-oxide compound. The formation of a similar inter-oxide phase was presumed for VOx-ZrO_2 on the basis of the TPR profile.

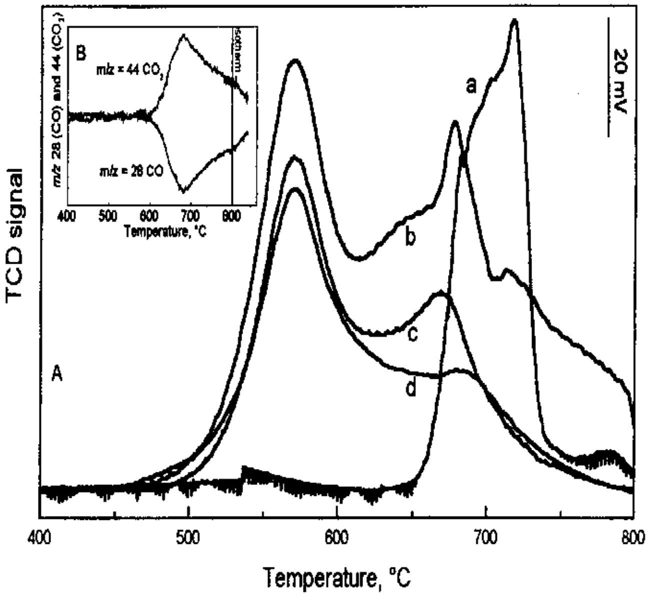


Fig. 2 A – Temperature programmed reduction of VOx-SiO_2-silica by H_2; B – Temperature programmed reduction of VOx-SiO_2– silica by CO; a – unsupported V_2O_5 — the intensity of spectra multipled by 0.3×; b – sample containing 1.12 wt.% of V; c, d – catalyst (0.73 wt. % of V) pretreated in O_2 (c) or in CO (d)

The sample containing bulk V_2O_5 (1.12 wt.% of vanadium) supported on SiO_2– silica was prepared by impregnation method. This sample was tested for redox behaviour by means of H_2-TPR (pattern b in Fig. 2A). The reduction profile exhibits at least four peaks: two peaks similar to reduction pattern of VOx-catalyst and two new sharp peaks superimposed on the profile of high-temperature peak at 675 and 715 °C. The intensity of newly observed peaks is low and they can be assigned to reduction of bulk V_2O_5 oxide on the surface of silica (below).

The reduction of unsupported V_2O_5 oxide was tested by means of H_2-TPR (pattern a in Fig. 2A). The reduction proceeds in two step (up to the temperature of 800 °C), but the peaks are almost overlapped. The observed reduction is probably proceeding as $V_2O_5 \rightarrow 1/3\ V_6O_{13} \rightarrow 2\,VO_2$ [13]. Due to the absence of the sharp peaks assigned to the reduction of V_2O_5 bulk oxide on the reduction profile of any the VOx-supported catalyst containing theoretically 1 wt.% of vanadium, it is possible to rule out the presence of this bulk particles on the surface of the prepared VOx-catalysts.

The temperature programmed reduction of VOx-SiO_2– silica catalyst by hydrogen was tested also after the treatment of the catalyst in carbon monoxide (2 hrs. in 5 vol.% CO in He at 800 °C). The temperature programmed reduction of this catalyst by CO is illustrated in Fig. 2B. The reduction by CO started at the temperature of 600 °C and until 800 °C it was still proceeding. The consumption of CO was accompanied by CO_2 formation. The H_2-TPR was carried out after this pretreatment. The resulting pattern (d) is presented in Fig. 2A. The reduction profile also exhibits two peaks, but the area of the higher-temperature peak was lowered substantially compared to the area of the pattern (c) (see Table I).

Oxidative Dehydrogenation of Propane

The comparison of the catalytic activity of supported VOx catalysts was performed using the same reaction temperature (450 °C) and sample weight (1 g). The conversion (X) of propane was obtained in the range from 2.6 to 15 %, conversion of oxygen was higher compared to that of propane. Surprisingly, we achieved 100 % conversion of oxygen only for VOx-ZrO_2 catalyst, over the others it did not exceed 30 %. The activity of catalysts was changing with time-on-stream. Conversion was decreasing and selectivity for propen was increasing, therefore a certain time-on-stream (TOS = 200 min) was chosen for comparison of catalytic behaviour in C_3-ODH reaction. Propene and carbon oxides were detected as main reaction products. The products of cracking *i.e.* methane and ethane were detected only in trace concentrations and their selectivities (*S*) did not exceed 0.5 %. Aromatics (benzene and toluene – selectivity for both under 3 %) were detected in the case of the most acidic catalysts (SiO_2). There are differences in activity between VOx catalysts. Propene is the main product for both VOx-SiO_2 catalysts (selectivity 64 and 75 %), and production of CO_2 by total combustion is low (S_{CO_2} = 5 – 6 %). On the other hand, carbon oxides (COx) are mainly produced by catalysts supported on MgO (highest selectivity to CO_2) and ZrO_2 (highest selectivity to CO). The experimental data of propane and oxygen conversion and selectivity for the main reaction products for the time-on-stream of 200 min and propene selectivity for propane conversion 5% are sumarized in Table II.

The 5 % conversion was obtained in different TOS for different catalysts due to partial deactivation during the reaction. The propane conversion values at TOS = 200 min were recalculated to reaction rate (*rr*) data using aproximative

Table II Results of catalytic activity test for propane oxidative dehydrogenation at 450 °C after 200 min in the reaction stream

Support	X_{O_2}, %	$X_{C_2H_8}$, %	$X_{C_3H_6}$, %	S_{CO}, %	S_{CO_2}, %	$S_{C_3H_6}$[a], %	log *rr*[c]
SiO_2 – silica	6.1	4.4	64.1	27.3	5.6	63.2	2.77
SiO_2 – aerosil	2.8	2.6	74.8	19.4	5.8	61.1	2.54
TiO_2 – anatase	25.1	8.8	59.4	27.2	13.4	62.0	3.06
Al_2O_3 – γ-alumina	7.2	5.6	54.8	32.2	12.9	57.1	2.87
ZrO_2	100.0	15.0	21.3	60.9	17.8	b	3.30
MgO	11.1	3.9	16.3	38.7	45.0	15.0	2.71

[a] propene selectivity for 5 % propane conversion
[b] 5 % propane conversion not reached
[c] calculated from Eq. (1) for TOS = 200 min

equation (1); these data are reported in Table II. The values of reaction rate give similar information as conversion of propane in reference to the fact that *w*/*F* ratio is constant for all the catalysts. These values were used for comparison with data obtained in crotonaldehyde partial oxidation investigation

$$rr = \frac{dX}{d\left(\frac{w_{cat}}{F^0_{CA}}\right)} \approx \frac{X}{\left(\frac{w_{cat}}{F^0_{CA}}\right)} \qquad (1)$$

Crotonaldehyde Oxidation

The catalytic activity tests were carried out in the temperature range of 260 – 420 °C. Maleic anhydride, furan and carbon oxides were detected as main reaction products. Other reaction products as crotonic acid, maleic acid, furan-2(5H)-one, furan-2(3H)-one, acetaldehyde, acetic acid, and acrolein, were detected, but the selectivity for these products did not exceed 3 %. Except for these products, the formation of unidentified polymeric compound was observed in compliance with Ref. [14]. The total amount of the products of the polymerization was not determined quantitavely. It was found that crotonaldehyde consist of two isomers separated by gas chromatography. These isomers were identified as *cis*-crotonaldehyde (2*Z*) and *trans*-crotonaldehyde (2*E*). Their catalytic isomerization reaction takes place over all the catalyst investigated.

The highest conversion of crotonaldehyde was measured on the SiO_2 and TiO_2 supported catalysts when its value reached 80 %. The maximum oxygen conversion was nearly 100 % in these cases. The other catalysts were substantially less active. The selectivity for furan was the highest with the SiO_2 supported catalysts (14 %). The selectivity for maleic anhydride exhibited maxima for TiO_2 and ZrO_2 supported catalysts (19 %). Only small amount of the products of partial oxidation was detected on the VOx - MgO supported catalyst. This catalyst produced only polymerization products in the whole temperature region. The experimental data of oxygen and crotonaldehyde conversion and selectivity for the main reaction products at 360 °C with all the supports used are summarised in Table III.

The crotonaldehyde conversion values were recalculated to the reaction rates (*rr*) using the approximate equation (1) as in the case of C_3-ODH. The obtained values of crotonaldehyde conversion at 280 °C, together with the corresponding values of the reaction rate values are presented in the Table III. The mean values of the activation energy of the reaction were calculated using the slo-

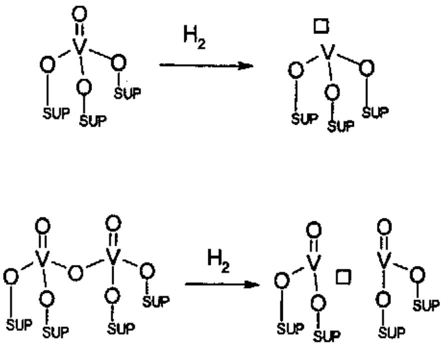
Table III Results of catalytic activity test of VOx catalysts at 360 °C and conversion of crotonaldehyde and corresponding values of reaction rate at 280 °C and the activation energy of partial oxidation of crotonaldehyde from Arrhenius plot for various supports

Support	360 °C					280 °C		
	X_{O_2}, %	X_{CA}, %	S_{FU}, %	S_{MA}, %	S_{CO_x}, %	X_{CA}, %	$\log rr$	E_A, kJ mol^{-1}
SiO_2 – silica	97	77	14	5	60	42.5	1.557	77.8
SiO_2 – aerosil	99	73	14	4	65	39.3	1.480	84.7
TiO_2 – anatase	98	80	14	19	46	18.7	0.740	105.2
ZrO_2	66	54	8	19	46	5.2	–0.855	97.2
Al_2O_3 – γ alumina	68	35	0	4	82	2.0	–1.516	108.0
MgO	2	7	0	1	0	0.4	–3.061	110.2

pe of so-called Arrhenius plot (*i.e.* dependence $\ln rr \sim 1/T$, data not presented) in temperature region for crotonaldehyde conversion less than 40 %. The activation energies varied from 78 (SiO_2) to 110 kJ per mol (MgO) and their values are summarised in Table III.

Discussion

Description of catalysts is necessary for understanding of the processes proceeding on the catalytic system. The redox properties belong among the most important features of investigated catalysts. Redox behaviour was tested by means of H_2-TPR experiment (Figs 1 and 2). As mentioned above, the VOx units can exist on the surface as monomer, oligomer or bulk units. All these units exhibit different types of interaction with supports [15] and different properties with regard to hydrogen during H_2-TPR. The vanadium atoms connected by bridging oxygen in oligomeric units (V-O-V; denoted as iii) in introduction) were suggested to be reduced by weaker reduction agents (hydrocarbons, CO *etc.*) [2,5] and their bonding energies to supports are lower comparing to monomer [15]. Equivalent amount of CO_2 is produced during reduction of oligomeric units. Therefore, we measured H_2-TPR profile after pretreatment in CO or in oxygen. The reduction profile after CO pretreatment was different (Fig. 2) — the intensity of high-temperature peak was decreasing, although the intensity of low-temperature peak remained almost constant. Thus, the low-temperature peak could be assigned to the reduction of monomer VOx units (Scheme 1) and the high-temperature peak to reduction of oligomeric units in accordance with the calculation of Ferreira and Volpe [15]. Oligomeric VOx species can be reduced by hydrogen at higher temperatures, although these units were supposed to be reduced by weaker reduction agents and their bonding energies to supports are lower compared to the monomer [15,16], which could be explained by a lower value of the pre-exponential factor in the Arrhenius equation for reaction rate constant or by a ste-



Scheme 1 The assumed mechanism of the reduction of monomeric and oligomeric VOx species [15].

ric effect.

The acidity of catalysts is another important characteristics for the catalysts. One of the method used for comparing acidity of catalysts is the comparison of their isoelectric point (IEP) [12]. The IEP value is defined as the pH value when the surface of the catalyst is neutral in water suspension. The acidity sequence is: $V_2O_5 > SiO_2 >> TiO_2 > ZrO_2 > Al_2O_3 >> MgO$. The acid-base properties of supports influences dramatically population of monomer / oligomer VOx units on the surface. The dispersion is the lowest for highly acid SiO_2 supports (the area of high-temperature peak is highest), because the tendency of migration of acid VOx unit on the acid surface is low (see Table I). The other extreme is formation of inter-oxide phase between VOx and MgO. The presence of ortho- and pyrovanadates in similar catalytic systems is mentioned in Refs [6,11,12], but unfortunately, we do not have enough data to distinguish them.

Both the reaction rate of crotonaldehyde partial oxidation at 280 °C and the reaction rate of C_3-ODH depend on the population of the vanadium oxide species on the surface of the catalyst. This dependence is illustrated in Fig. 3, where it can be clearly seen that the oligomeric species play a significantly different role in the two reactions studied. The slopes of these linear dependencies are close to the value of 0.5 for partial oxidation of crotonaldehyde and –0.5 for C_3-ODH. Therefore, the reaction rate is proportional to the square root of the number of oligomeric species (L_2 — detected as the relative area of the high-temperature peak in the H_2-TPR profile) in the case of CA oxidation or to reciprocal value of the square root of L_2 in the case of C_3-ODH. It means that the oligomeric species play the role of the active sites in partial oxidation of CA, but increasing of their concentration decreases the activity of the catalysts in C_3-ODH reaction, and the-

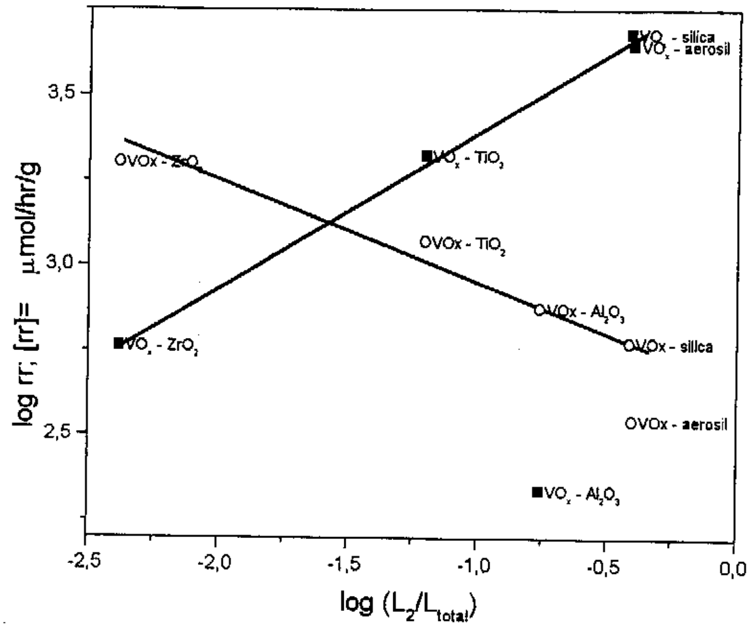


Fig. 3 The logarithm of reaction rates of both the C_3-ODH and CA partial oxidation versus the logarithm of the relative amount of VOx oligomers on the catalyst surface. Empty markers – C_3-ODH, solid markers – CA partial oxidation

refore the monomeric VOx units may be denoted as the active species for this reaction [1,2].

It was observed during the experiments on bulk oxide systems that catalysts treated under similar reaction conditions are completely in reduced state (will be published elsewhere). It means that the reoxidation of catalysts can be taken as the rate limiting step at least for bulk oxides. Moreover the dependence of *rr* on the square root of population of the oligomers can be ascribed to dissociation mechanism to adsorption of molecular oxygen, and we can assume that the reoxidation of the catalyst is the rate-limiting step for both studied reaction too [2,11]. Because the transport of oxygen through lattice of catalyst is not possible in the case of supported monomeric VOx species, it is necessary to expect another mechanism of transport of the dissociated oxygen, probably *via* spill-over mechanism. The catalyst with higher concentration of oligomeric units can suppress this type of oxygen transport through possible trapping of the migrating dissociated oxygen atoms.

The Mars–van Krevelen mechanism [7] is generally accepted for both reactions taking place on VOx-based catalysts. One of the important steps in the mentioned mechanism is the reoxidation of the active species of the catalyst in re-

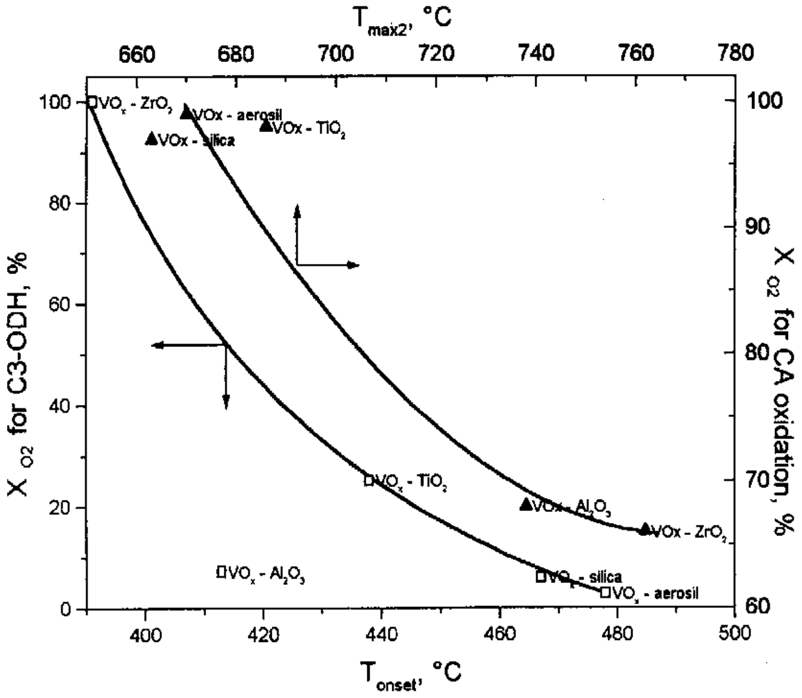


Fig. 4 The dependence of the conversion of oxygen in the C_3-ODH reaction as a function of onset temperature H_2-TPR and the dependence of the conversion of oxygen in the CA partial oxidation on temparature of maxima of second TPR peak. Empty markers – C_3-ODH, solid markers – crotonaldehyde (CA) partial oxidation

duced state. It is necessary to study oxygen conversion in relation to the behaviour of the active species. The correlation between oxygen conversion and results from H_2-TPR are presented in Fig. 4. The most easily reducible catalysts (onset temperature from H_2-TPR) show the highest oxygen conversion in the C_3-ODH reaction. On the other hand, the correlation between the onset temperature and the O_2 conversion for partial oxidation of CA was not found, but there is a correlation between the reduction of oligomer VOx units (high-temperature peak) and the conversion of oxygen (Fig. 4).

The activity of catalysts is mainly affected by redox properties of VOx species; on the other hand, the selectivity for the required main products is controlled by acid-base properties of the supports (represented by the value of the isoelectric point — IEP) (Fig. 5). The catalysts with the lowest values of IEP (the most acidic ones) exhibited the highest selectivity for the products of both oxidative dehydrogenation reactions — propene for C_3-ODH reaction (over 60 %) or furan (S_{FU} = 14 %) for CA oxidation. The selectivity for maleic anhydride

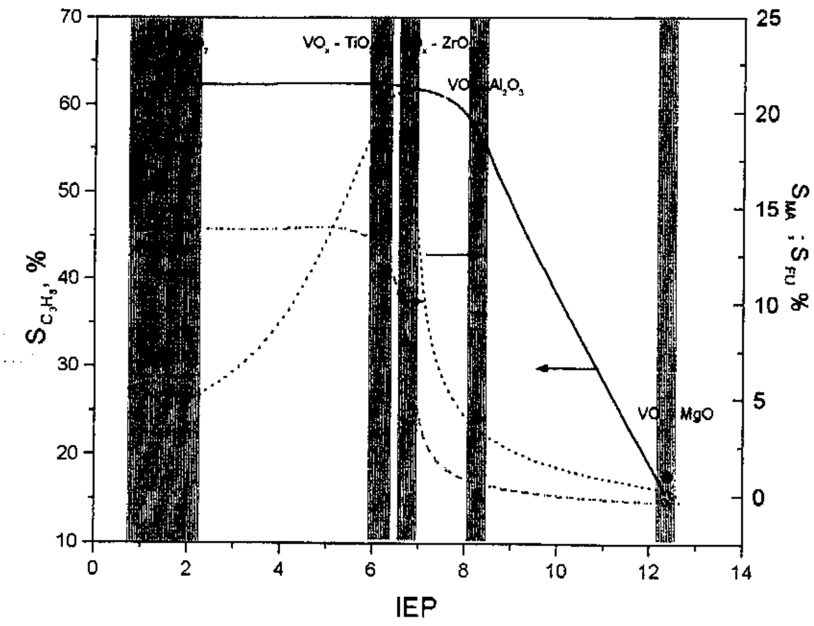


Fig. 5 The dependence of selectivity for the main reaction products for both the C_3-ODH (propene) and CA partial oxidation (furan and maleic anhydride) on an isoelectric point (IEP) of supports. Empty markers – C_3-ODH, solid markers – CA partial oxidation.

exhibits a maximum for VOx units supported on neutral oxides (TiO_2 or ZrO_2). This effect can be ascribed to strong interaction of the organic molecule to the acid site of the catalyst. The main products of the oxidative dehydrogenation reactions (propene and furan) act as bases, and their mobility on the acid surface is suppressed, protecting them from overoxidation to CO_x or maleic anhydride. A similar effect may explain the maleic anhydride selectivity dependence on the IEP of support.

The isomerization of crotonaldehyde was experimentally proved during the catalytic tests. Moreover, the acid supports can affect the rate of such isomerization reaction when the *cis*-isomer plays the role of a plausible intermediate for the furan formation which can be subsequently oxidized to maleic anhydride; the *trans*-isomer can be oxidized to the crotonic acid and subsequently to maleic anhydride *via* partial oxidation mechanism. The crotonic acid was detected as an intermediate in all the catalytic tests in small amount, except VOx – MgO catalyst testing. This fact allows us to make the assumption about a parallel character of oxidation of crotonaldehyde to maleic anhydride *via* both routes mentioned. This assumption can be supported by the dependence of the apparent activation energy of the partial oxidation of crotonaldehyde on the IEP, values

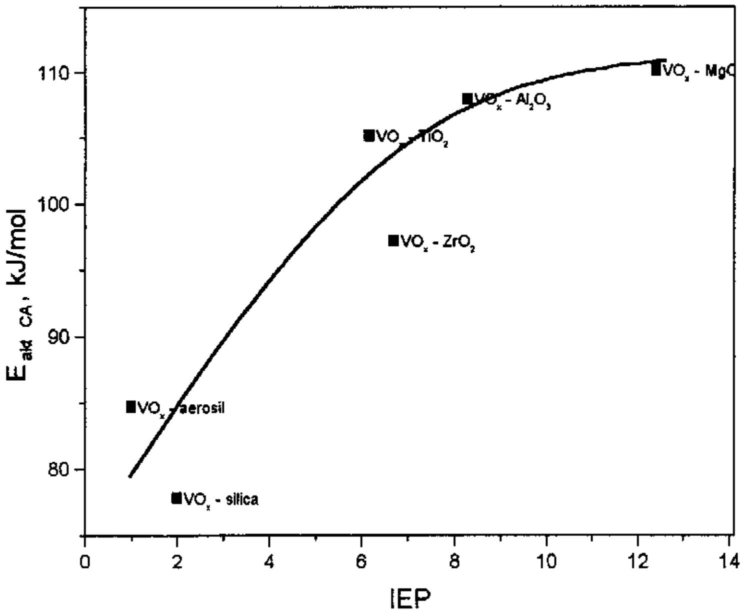
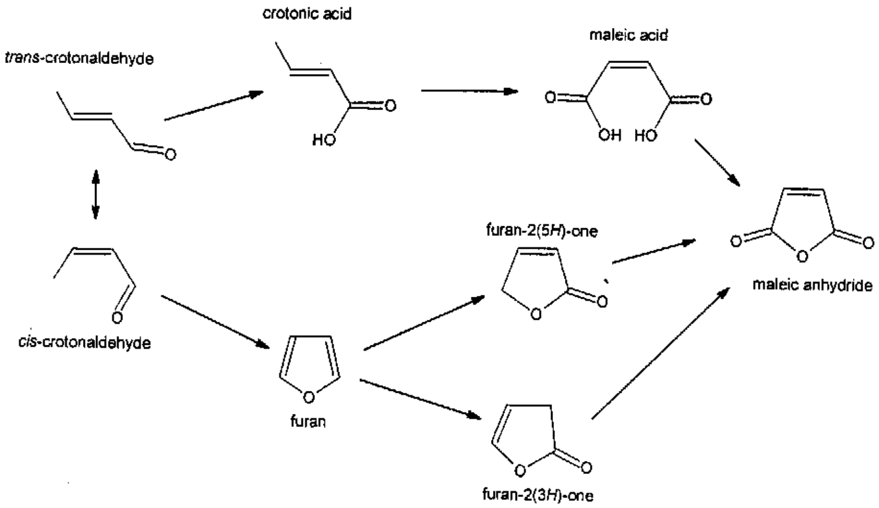


Fig. 6 The mean activation energy of crotonaldehyde partial oxidation in dependence on an isoelectric point (IEP) of supports taken from Ref. [12]

which is presented in Fig. 6. The lowest values (~80 kJ mol^{-1}) were observed for VOx catalysts supported on SiO_2 (*i.e.* the most acid catalyst); then the values increase together with increasing IEP of the support. The maximum value (115 kJ mol^{-1}) was reached for VOx supported on MgO. Significant difference in values of activation energy allow an assumption about simultaneous occurence of at least two different reaction pathways which compose the final value of mean activation energy. Hence, we suggest the following reaction scheme based on the detected reaction compounds (Scheme 2).

Conclusion

- The monomeric or oligomeric units of VOx can be distinguished by means of H_2-TPR. The redox properties of these species are affected by the support: monomeric units are reduced by hydrogen at lower temperature and oligomeric VOx units are detected as high-temperature peak on H_2-TPR profile. The bulk V_2O_5 was not observed on the surface of the catalysts. The inter-oxide compounds were formed in the case of MgO oxide.
- The monomeric and oligomeric units play different roles in propane oxidative



Scheme 2

dehydrogenation and CA partial oxidation: monomeric units are active in oxidative dehydrogenation of propane, and oligomeric VOx units are active in partial oxidation of crotonaldehyde in both the furan and maleic anhydride formation. The catalytic activity of these species is correlated with their redox properties.

- The selectivity for the main reaction products is controlled by the acid-base properties of the supporting materials: selectivities for the products of oxidative dehydrogenation are the highest with the most acid catalyst, whereas the highest selectivity for maleic anhydride is achieved with neutral catalyst.
- The reaction scheme of crotonaldehyde partial oxidation is sugessted. The formation of furan proceeds *via* the oxidative dehydrogenation of *cis*-crotonaldehyde on the acid site of the catalyst, followed by the possible subsequent oxidation of furan to maleic anhydride. The partial oxidation of crotonaldehyde *via* crotonic acid is the second parallel route of the formation of maleic anhydride.

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