Editor's choice paper

n-Butane oxidative dehydrogenation over VO$_X$-HMS catalyst

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ABSTRACT

The demand for olefins increases in recent years. Oxidative dehydrogenation (ODH) of n-butane is possible alternative to classical dehydrogenation, steam cracking and fluid catalytic cracking processes. The role of particular VO$_X$ species supported on hexagonal mesoporous silica (HMS) in oxidative dehydrogenation (ODH) of n-butane was investigated on two sets of VO$_X$-HMS catalysts prepared by wet impregnation and direct synthesis differing in amount and distribution of VO$_X$ species. The materials were characterized by XRF, N$_2$-BET isotherms, XRD, SEM, H$_2$-TPR, O$_2$-TPO and DR UV–vis spectroscopy and tested in ODH of n-butane in the range of temperature from 460 to 540 °C. The highest activity and selectivity to olefins were reached on materials with high content of isolated monomeric VO$_X$ units with tetrahedral coordination which are generated up to 4–5 wt.% of vanadium. The species with high degree of polymerization participate mainly on total oxidation reactions and those species are formed especially by wet impregnation.

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1. Introduction

Main task of today's chemical industry is a production of a large amount of organic compounds. Presently it is very important to find alternative processes for production of these compounds from more economically suitable raw materials and with smaller impact to environment. For example we can use alkanes instead alkenes because alkanes are by half cheaper compared to alkenes which are easily available [1]. The global demand for C$_4$-olefins increases in recent years. In the year 1984 the world production of butenes was 28.1 mil. tons [2]. In the year 2004 it was already 44 mil. tons [3]. Similar situation is in the case of 1,3-butadiene whose production was 1.3 mil. tons in the year 1983 in the USA [2] and nearly 2.1 mil. tons in year 2000 [4].

Oxidative dehydrogenation (ODH) of n-butane is an alternative to classical dehydrogenation, steam cracking and fluid catalytic cracking processes. The ODH reaction is thermodynamically favorable and can be proceed at temperature much lower compared to a non-oxidative dehydrogenation. To a certain extent, the conditions of ODH reaction reduce the problems of coke formation and catalyst deactivation. But this reaction has still several unresolved problems whose hinder its industrial use. The molecule of butane contains four carbon atoms which enable a lot of consecutive reactions. This makes possible the formation of lot of consecutive reaction products as described in Ref. [5]. Moreover the formed alkenes are approximately four times more reactive then butane [6]. It causes the decrease of selectivity to asked products with the increasing conversion of butane. Thus the development of suitable catalyst is still important challenge.

Vanadium oxide based catalysts are very often used as catalysts in ODH reaction. Their employment offers several advantages: lower temperature for the activation of C–H bonds of reactants (limitation of cracking and combustion reactions) and suitable geometric and electron structure of VO$_X$ (tunable with used matrix or temperature). The vanadium-oxide catalysts are hence suitable for insertion oxygen atom to molecule hydrocarbon. On the other hand vanadium oxide catalysts cannot be used in its bulk form (leads to non-selective reactions) but have to be used as the well dispersed VO$_X$ species supported on the suitable support [6–8].

The support strongly affects the catalytic performance. The textural properties and acid–base character of the support are the most important factors [1]. The acid–base character has influence on (i) the dispersion of the vanadium oxides [7,9] (ii) their structure [7,9] and (iii) retention period of reactants and reaction intermediates on the surface [6,7,10]. From this point of view the MgO support (iso-electric point (IEP) ca. 12.5 [7]) seems as the best support for ODH of alkanes because rising alkenes (more basic then alkanes) are easy desorbed and it suppress consecutive reactions leading to CO$_X$. Moreover acid character of V$_2$O$_5$ (IEP 1.4 [7]) facilitates good dispersion of VO$_X$ species. On the other hand MgO supports have area only about 100–150 m^2 g^{-1} [11–13] what limits attainable vanadium loading. From this reason is required to find new support materials with large surface.

The vanadium oxide (VO$_X$) units supported on the surface of amorphous SiO$_2$ or ordered mesoporous silica (SBA-15) [14–16]

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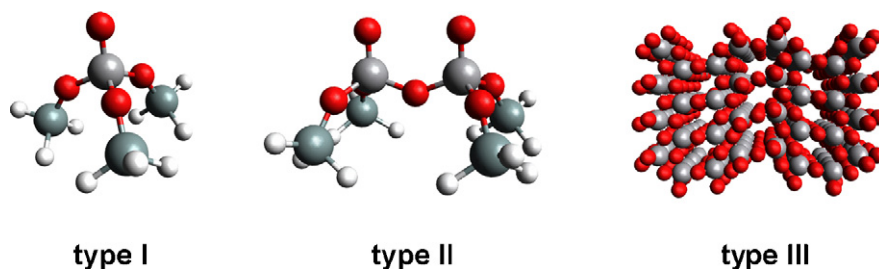
Scheme 1. Three different type of VO_X species exist on the HMS surface. Type I – isolated monomeric units with tetrahedral coordination, type II – one-dimensional oligomeric units with distorted tetrahedral coordination and type III – two- and three-dimensional polymeric units in octahedral coordination.

were reported to be potentially suitable catalysts in the ODH of *n*-butane in the past. The hexagonal mesoporous silica (HMS) is used as support in this work. Advantages of the supported catalysts on the HMS are: larger surface area (a good dispersion of active particles), thermal stability, good mechanical properties, weak acid centers, system of one dimensional open channels with 35–40 Å pore diameter (easy mass transport of products) [17,18]. VO_X particle might be present at surface of catalysts in four different forms: highly dispersed isolated monomeric units with tetrahedral coordination $(sup-O)_3V=O$ (sup – atom of support) (type I – see Scheme 1), one-dimensional oligomeric units connected by V–O–V bonds up to distorted tetrahedral coordination (type II – see Scheme 1), two-dimensional polymeric units in octahedral coordination called oxide-like species (type III – Scheme 1) and bulk three-dimensional V_2O_5 crystallites (type IV) [6,19].

The method of the deposition of active vanadium phase strongly influences the nature and abundance of rising VO_X species. The simple wet impregnation method of vanadium salt (NH_4VO_3, vanadyl sulfate, vanadyl acetylacetonate) is very often used for the deposition of VO_X species [14,20–23]. However, impregnation methods very often lead to materials with broad distribution of VO_X species including the VO_X units with a low degree of dispersion or bulk oxide. The direct hydrothermal synthesis of mesoporous vanadosilicate is an alternative method for incorporation of vanadium species on the silica surface by the introduction of the required amounts of metal salt to the synthesis gel. Despite of a great progress in the development of advanced method for direct synthesis of functionalized mesoporous silicas [24–26] but the exact description and mastery this synthesis is still great challenge.

In the present paper, we report for the first time the comparison of VO_X-HMS prepared by wet impregnation and direct synthesis as potential catalysts for ODH of *n*-butane and we want to contribute to understanding of relationship between vanadium structure on the HMS support and activity in ODH of *n*-butane. To analyze the effect of vanadium concentration on the type of VO_X structure, on dispersion of VO_X and their catalytic activity, the catalysts were characterized by different techniques (XRF, N_2-adsorption, XRD, DR UV–vis and H_2-TPR).

2. Experimental

2.1. Preparation of catalysts

Catalysts have been prepared in two ways (i) by impregnation and (ii) by direct synthesis. The hexagonal mesoporous silica (HMS) was used as support in both cases. The HMS was synthesized at ambient conditions according to the procedure reported by Tanev [27] by using dodecylamine (DDA, Aldrich) as a neutral structure directing agent in the mixture of ethanol and re-distilled water. After 20 min of homogenization was added tetraethylorthosilicate (TEOS, Aldrich) as a silica precursor. The reaction mixture was stirred at RT for 18 h. The solid product was filtered, washed

by ethanol and calcined in air at 450 °C for 20 h (with heating rate 1 °C/min) for the template removal. The various amount (0.5–15.7 wt.% of V) of vanadium oxo-species was introduced onto the silica support by the wet impregnation from EtOH solution of vanadyl acetylacetonate for the first set of catalysts. Impregnated samples were dried at 120 °C in air overnight and then calcined at 600 °C in air for 8 h (with heating rate 5 °C/min).

The set of synthesized VO_X-HMS catalysts (1.2–14.0 wt.% of V) was prepared by direct-synthesis method which was based on work published by Reddy and Sayari [28]. The procedure was the same as in the case of the HMS synthesis when the ethanol solution with desired amount of $VO(acac)_2$ was added to the reaction mixture (DDA, H_2O and ethanol) during the synthesis. Following procedure was similar to HMS preparation. Finally, the solid was calcined in flow of air at 450 °C for 20 h (with heating rate 1 °C/min).

The investigated samples were denoted as I-VHMS-*x* and S-VHMS-*x* for impregnated and synthesized samples, respectively, where *x* is the vanadium content in weight percentage of V.

2.2. Elemental analysis

The vanadium content was determined by means of ED XRF by ElvaX (Elvatech, Ukraine) equipped with Pd anode. Samples were measured against the model samples (a mechanical mixture of pure SiO_2 and $NaVO_3$) of granulated to the same size as catalysts.

2.3. Textural properties

The N_2-adsorption isotherms were obtained at 77 K using the through-flow chromatographic method. The relative pressure of nitrogen was varied in the range of 0.01–0.30. The specific surface area (S_{BET}) was determined by the fitting of the experimental data to the BET isotherm. The surface vanadium density (VO_X surface density, VO_X nm^{-2}) was calculated according to:

$$\text{Surface density} = \frac{N_A w_V}{M_V S_{BET}} \cdot 10^{-18} \tag{1}$$

where N_A is Avogadro constant, w_V mass fraction of vanadium in V-HMS (wt.%), M_V is molecular weight of vanadium (50.94 g mol^{-1}) and S_{BET} is the specific surface area of V-HMS catalyst (m^2 g^{-1}).

The structure and crystallinity of catalysts was probed by X-ray diffraction (D8-Advance diffractometer, Bruker AXE, Germany) in the 2θ range of 2–35° with Cu Kα radiation ($\lambda = 1.5406$ Å) and scanning electron microscopy (SEM) using JSM-5500LV microscope (JEOL, Japan).

2.4. DR-UV–vis spectroscopy

UV–vis diffuse reflectance spectra were measured using the Cintra 303 spectrometer (GBC Scientific Equipment, Australia) equipped with a Spectralon^{TM} – coated integrating sphere using a Spectralon^{TM} discs as a standard. The spectra were recorded in

the range of the wavelength 200–850 nm. Before the spectra measurement the samples were dehydrated and oxidized in the glass apparatus under static oxygen atmosphere in two steps: 120 °C for 30 min and 450 °C for 60 min and subsequently cooled down to 250 °C and evacuated for 30 min. After the evacuation the samples were transferred into the quartz optical cuvette 5 mm thick and sealed under vacuum. For additional details you can see Ref. [22]. This procedure guaranteed complete dehydration and defined oxidation state of vanadium for all catalysts. The obtained reflectance spectra were transformed into the dependencies of Kubelka–Munk function $F(R_\infty)$ on the absorption energy $h\nu$ using the equation:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{2}$$

where R_∞ is the measured diffuse reflectance from a semi-infinite layer [29].

2.5. H_2-TPR measurements

Hydrogen temperature programmed reduction (H_2-TPR) was used for study of redox behaviour and for distinguishing of individual VO_X species on the surface and the AutoChem 2920 (Micromeritics, USA) was used for the measuring. A 100 mg sample in a quartz U-tube micro reactor was oxidized in oxygen flow at 450 °C (2 h). The reduction was carried out from 30 °C to 900 °C with a temperature gradient of 10 °C/min in flow of reducing gas (5 vol.% H_2 in Ar). The changes in hydrogen concentration were monitored on TCD detector and simultaneously hydrogen consumption and water formation was detected on quadruple mass spectrometer OmniStar™ GDS 300 (Pfeiffer vacuum, Germany). The temperature programmed oxidation (TPO) experiments with the sample S-VHMS-4.9 were performed by the same apparatus. The 100 mg of sample was pre-reduced in the gas mixture (5 vol.% H_2 in Ar) as in the case of TPR. The oxidation was carried out using the gaseous mixture (2 vol.% O_2 in He) and various heating rates 8, 12 and 20 °C/min to obtain the apparent re-oxidation activation energy E_A using the Kissinger equation [30]:

$$2 \ln T_{max} - \ln \beta = \frac{E_A}{RT_{max}} + \text{const} \tag{3}$$

where T_{max} is the temperature of the maximum of oxidation peak determined at particular heating rate β.

2.6. Catalytic tests in ODH reaction

The n-butane ODH reaction was carried out in a glass plug-flow fixed-bed reactor at atmospheric pressure in the kinetic region (independently checked) and under steady state conditions of reaction. Typically 400 mg of catalyst (grains 0.25–0.50 mm) was diluted with 3 cm³ inert SiC to avoid the catalytic bed overheating. The catalysts were pre-treated in the oxygen flow at 450 °C for 2 h before each reaction run. The input feed composition was $C_4H_{10}/O_2/He = 10/10/80$ vol.% – with a total flow rate of 100 cm³ min⁻¹. The catalytic activity was compared in the range 460–540 °C at the steady state conditions. The composition of reaction mixture analysis was made by on-line gas-chromatograph CHROM-5 (Laboratorni pristroje Praha) equipped with a thermal conductivity detector (TCD) for permanent gases and flame ionization detector (FID) for combustible products of ODH reaction. The n-butane and products of ODH reaction (butadiene, 1-butene, cis-2-butene, trans-2-butene, propene and propane) were separated using a packed column with n-octane on ResSil™ (Restek) at 20 °C. The packed column Porapak Q (Supelco) was used for the analysis of ethane, ethene, CO_2 and acetaldehyde. The molecular sieve 13X (Supelco) was used for the separation of permanent gases.
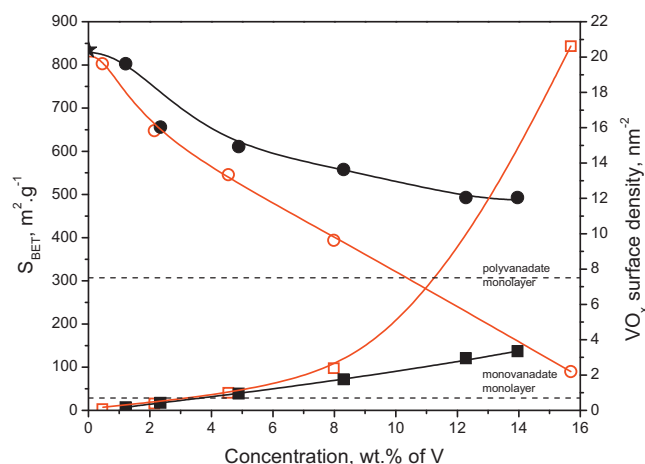

Fig. 1. Dependence of specific surface area (ring) and VO_X surface density on vanadium concentration (square) for synthesized (full symbol) and impregnated (empty symbol) V-HMS samples.

The conversion was calculated using following equation:

$$X_i = \frac{n_{i0} - n_i}{n_{i0}} \cdot 100 \tag{4}$$

where n_{i0} is amount of key component in the input feed and n_i is the amount of key component in the output from reactor.

The selectivity to products was calculated as:

$$S_j = \frac{\nu_j \cdot n_j}{\nu_i \cdot (n_{i0} - n_i)} \cdot 100 \tag{5}$$

where ν_i, ν_j is number of carbon atoms of starting compound resp. products, n_{i0} is molecular amount of key component in the input feed, n_i is the molecular amount of key component in the output and n_j is the molecular amount of product in the output from reactor.

Yield was calculated according to Sachtler [31]. The productivity and turn-over-frequency (TOF) values per V atom was calculated based on mass balance of the carbon. The TOF values were calculated as:

$$\text{TOF} = \frac{n_{n\text{-}C_4}^0 X_{n\text{-}C_4} M_V}{m_{cat} w_V} \tag{6}$$

where $n_{n\text{-}C_4}^0$ is mol. flow n-butane (mol s⁻¹), $X_{n\text{-}C4}$ conversion of n-butane (%), M_V is molar weight of vanadium (50.94 g mol⁻¹), m_{cat} is weight of catalyst (g), w_v is mass fraction of vanadium in catalysts.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. Textural properties

The HMS materials provide the isotherm of type IV with hysteresis loop of type H4 which is typical for combination micro- and mesoporous system of channels [20]. The average pore diameter of pure HMS support was 4.2 nm with the mesopore volume 0.68 cm³ g⁻¹ and specific surface BET 835 m² g⁻¹. Both sets of the catalysts exhibit significant decrease of the S_{BET} value with increasing vanadium loading especially in the case of samples prepared by the impregnation method where the sample containing 15.7 wt.% of vanadium had a S_{BET} value ca. only 90 m² g⁻¹. The decrease of surface for the synthesized samples was only in the range from 800 to 490 m² g⁻¹. The dependence of surface decrease on concentration is shown in Fig. 1. This behaviour can be attributed to partial destruction of the framework [21,22] or deposition of vanadium oxo-species into mesopores which partially blocks these
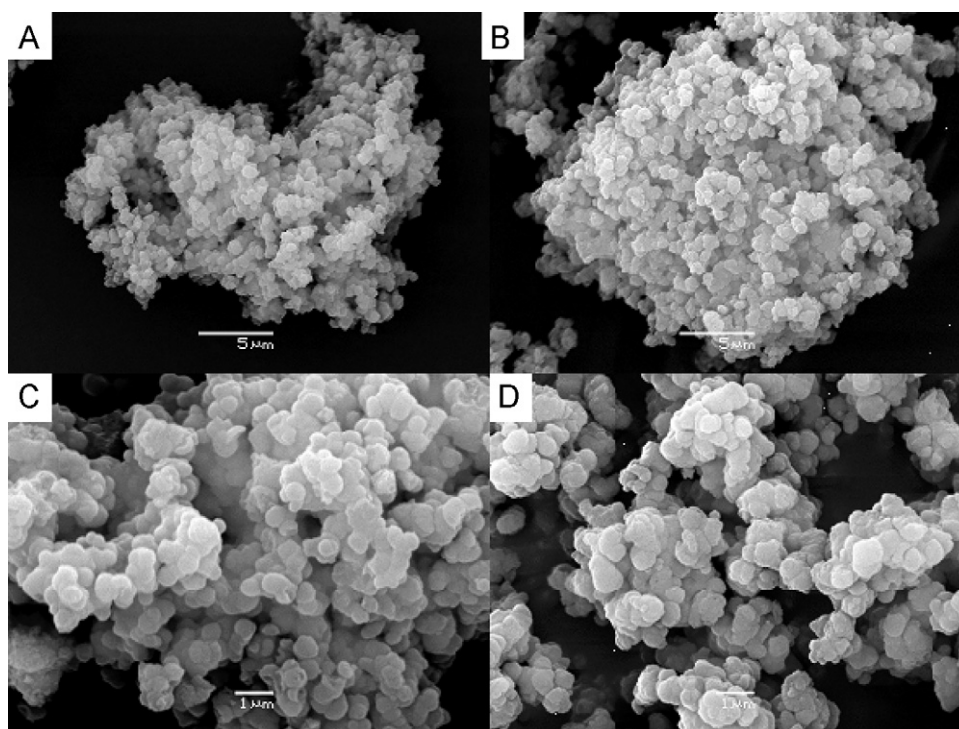
Fig. 2. SEM images of V-HMS catalysts prepared by wet impregnation (sample I-VHMS-4.6, pictures A and C) and direct synthesis (S-VHMS-4.9 sample, pictures B and D).

pores [14,22]. On the other hand decrease in surface areas can indicate that the VO_X species are located inside the channel system on the inner walls of mesoporous matrix.

The abundance of various vanadium oxide species on the surface of silica based supports was previously related to the surface concentration of VO_X species whose values are summarized in Table 1. The value of 0.7 VO_X per nm^2 [32,33] is assumed to be a limiting value for the preferential formation of isolated monomeric units. The formation of various oligomeric and polymeric species is expected after reaching this value.

This value of the surface density was reached for samples containing more than 4 wt.% of vanadium for both sets of investigated catalysts (see Fig. 1). The 3D bulk oxide species were formed after reaching the surface VO_X density higher than 10 VO_X [8] or 7–8 VO_X units per nm^2 [32]. Hence it can be seen that only impregnated samples with highest concentration of vanadium contain higher detectable concentration of these species. These results correspond well with the information obtained from DR UV–vis spectroscopy.

The representative SEM images of impregnated (I-VHMS-4.6, Fig. 2)A and C and synthesized V-HMS samples (S-VHMS-4.9, Fig. 2B and D) are presented in Fig. 2. Both types of materials exhibit similar morphology of particles. The size of the particles was analyzed using Gwyddion software based on derivation of gray-scale signal for determination of grains boundary and consecutively diameter of circle with similar area. Any significant difference in particle size distribution was not observed in individual samples. Size of particles exhibited Gaussian distribution from 0.2 to 0.8 μm. These primary particles form large aggregates with dimensions about 20–150 μm. Typical orthorhombic V_2O_5 needles were not observed in any sample. No V_2O_5 clusters were detected in SEM-EDX mapping of V content and the concentration of vanadium was spread homogeneously in all parts of catalyst grains except I-VHMS-15.7.

3.1.2. XRD analysis

Fig. 3 shows the small-angle XRD patterns, in the 2θ range of 2–35°, for pure HMS and V-HMS. The region of 2θ value higher

than 35° contain no signal hence it is not showed here. Each sample exhibits one low-angle diffraction peak with line at 2–3° attributable to a d_{100} diffraction (spacing about 4.4 nm) and the very broad peak with low intensity among 15–35°. In addition, a weak broad shoulder around the 6° can be seen at synthesized samples with high concentration of vanadium and we can attribute it to d_{210} diffraction. The peaks d_{100} and d_{210} are characteristics for the SiO_2 hexagonal ordered structure and the broad low-intensity peak in range 15–35° pertains to small amount of amorphous SiO_2 which is not organized to the HMS structure [21,34]. With rise in VO_X loading the d_{100} peak weakens in intensity and gradually disappears which is results of the partial blocking of mesopores by VO_X and the decline in long-range order of hexagonal ordered structure [14]. All the synthesized V-HMS catalysts do not contain crystallites V_2O_5 in whole range of concentrations. The impregnated V-HMS cata-
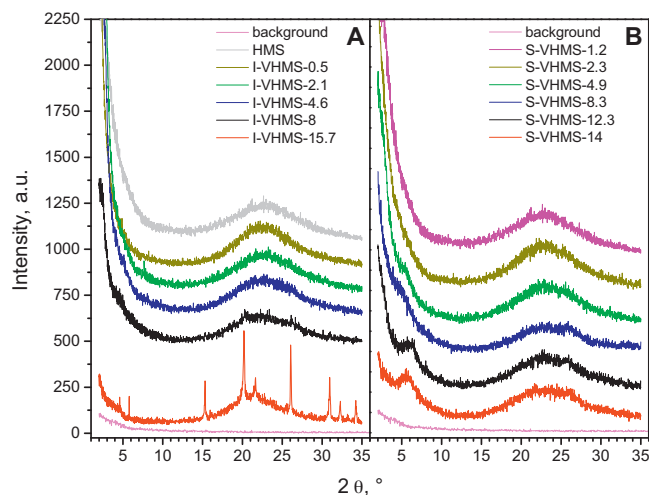

Fig. 3. X-ray diffraction patterns for V-HMS catalysts prepared by wet impregnation (A) and by direct synthesis (B).

Table 1
Chemical composition, results of physico-chemical characterization for both sets of investigated catalyst samples.

Sample name	c_V [a] (wt.%)	S_{BET} [b] (m² g⁻¹)	VO_X [c] (nm⁻²)	ε_0 [d] (eV)	X_{mono} [e]	T_{max} [f] (°C)	Δe [g]
S-VHMS-1.2	1.2	803	0.18	3.75	0.88	557	1.70
S-VHMS-2.3	2.3	636	0.43	3.74	0.87	575	1.76
S-VHMS-4.9	4.9	611	0.95	3.70	0.81	578	1.90
S-VHMS-8.3	8.3	558	1.76	3.57	0.62	592	1.74
S-VHMS-12.3	12.3	493	2.95	3.42	0.41	594	1.74
S-VHMS-14	14	493	3.35	3.38	0.37	591	1.68
I-VHMS-0.5	0.5	803	0.07	3.78	0.97	573	1.98
I-VHMS-2.1	2.1	648	0.39	3.73	0.85	563	2.14
I-VHMS-4.6	4.6	546	0.99	3.68	0.78	565	1.83
I-VHMS-8	8	394	2.39	3.50	0.52	577 (673)	1.97
I-VHMS-15.7	15.7	90	20.62	2.45	Not determined	595 (639)	1.87

[a] Vanadium content determined by XRF method.
[b] Specific surface area calculated following BET method.
[c] VO_X surface density (VO_X nm⁻²).
[d] Energy of absorption edge determined by Tauc [40].
[e] Relative amount of monomeric species determined from $\varepsilon_0 = 3.148 + 0.681X$.
[f] Position of first (second) maxima of H_2-TPR profile.
[g] Average change of oxidation state during H_2-TPR.

lysts up to loading of 8 wt.% of vanadium do not contain crystallites V_2O_5 as well but over this concentration reflections of bulk-like oxide VO_X species can be observed. It is represented by three main reflections at 15.4°, 20.2° and 26.1° in the XRD pattern (see Fig. 3) [14,20]. This observation is similar to results published by Karakoulia et al. [21] on V-HMS and V-MCM-41 who reported no presence bulk V_2O_5 up to 8 wt.% or on the V-SBA-15 materials studied by Liu [14]. Liu obtained the XRD signals of bulk oxides only when the concentration of vanadium was over 13.4 wt.% of vanadium. It can be said in conclusion that the presence or absence of V_2O_5 crystallites in the silica based VO_X catalysts depends on the preparation method of samples. These results are in a good agreement with the results from DR UV–vis spectroscopy as it will be discussed in next paragraph.

3.1.3. DR-UV–vis spectroscopy

Diffuse reflectance UV–vis spectroscopy provides information about the nature and oxidation state of vanadium. The spectra for both prepared sets of catalyst are presented in Fig. 4. The obtained spectra are similar to spectra published previously [20,22,26,35,36] for this catalytic system and contain several absorption bands at region 190-850 nm (6.5–1.46 eV) which are conventionally
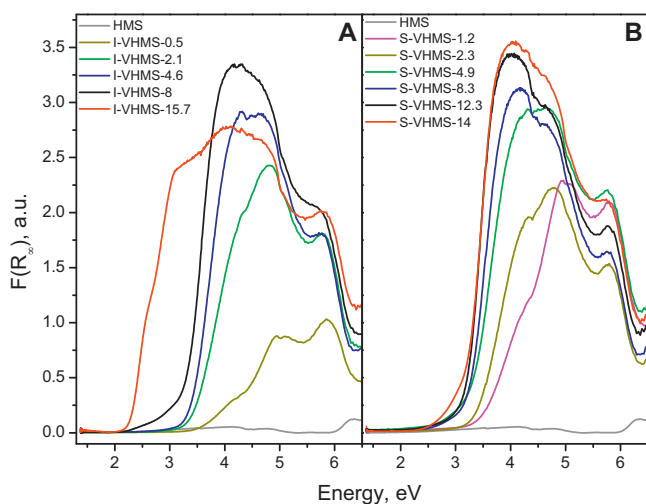

Fig. 4. Diffuse reflectance UV–vis spectra of dehydrated V-HMS samples prepared by wet impregnation (A) and direct synthesis (B). DR-UV–vis spectrum of pure HMS is displayed in both plots for comparison.

attributed to metal charge-transfer transitions of the $O \rightarrow V^{+V}$ type and d-d transitions of V^{+IV} [36].

The d–d absorption bands characteristic for the V^{+IV} in the region 1.55 – 2.07 eV [35] were not observed in any spectra. The broad obtained spectrum is superposition of several individual bands with poorly defined maxima. The region 4–6 eV is usually attributed to presence of isolated monomeric tetrahedrally (T_d) coordinated VO_X species (type I denoted in introduction) [22,26,37]. The second region 3–4 eV is attributed to presence of oligomeric distorted tetrahedral VO_X units (type II) [20,22]. The impregnated catalysts with vanadium loading over 8 wt.% exhibit band bellow 3 eV and it is attributed to 3D-octahedrally coordinated VO_X species (type III) [22,26]. The exact quantitative analysis or at least relative abundance of individual species is not possible to obtain due to broad and overlapping absorption bands and due to strongly nonlinear dependence of Kubelka-Munk function on the concentration of vanadium.

The method which can partially bypass this problem was developed for speciation of molybdenum oxide [38] and subsequently applied for vanadium oxide species on surface [23]. This method is based on the evaluation of absorption energy edge (ε_0) from UV–vis spectra using the expression introduced by Davis and Mott [39] or by Tauc [40] in the form:

$$(F(R_\infty) \cdot h\nu)^2 \propto (h\nu - \varepsilon_0) \tag{7}$$

Based on the empirical linear correlation of the referent compounds structure and the value of absorption energy edge Gao [23] suggested the possibility to obtain mean value of covalent V–O–V bonds (CVB) in the coordination sphere of central $V^{(+V)}$ cation and estimate degree of the polymerization of VO_X species.

Tian et al. [41] demonstrated that mechanic mixtures of sodium ortho-vanadate Na_3VO_4 (3.83 eV, model compound for isolated monomeric T_d units) and sodium meta-vanadate $NaVO_3$ (3.16 eV, standard for linearly polymerized T_d oligomeric units) exhibited linear dependence of the ε_0 value on the concentration of referent compounds and suggested this method for the determination of the relative amount of VO_X monomeric units denoted as X_m value. The values of ε_0 and the X_m of our samples are in Table 1. Disadvantage of this method is the fact that it cannot be used for materials which include higher content of the octahedrally coordinated VO_X bulk-like oxide species (for us the sample I-VHMS-15.7).

The samples with the vanadium concentration less than approximately 4-5 wt.% exhibit nearly the same linearly decreasing trend of the ε_0 value on the VO_X concentration and it depends less on the method of their preparation. When the vanadium loading reaches the value *ca.* 5 wt.% the samples prepared by the impregnation
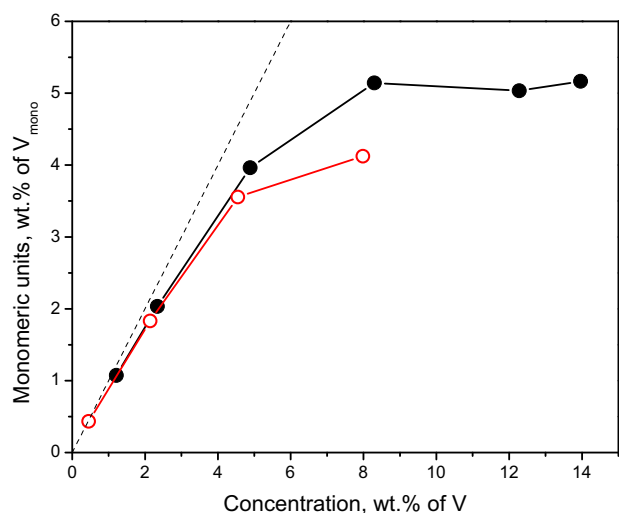
Fig. 5. The amount of monomeric species determined by Tian et al. [41] in dependence on vanadium loading for impregnated samples (open red points and red line) and for samples prepared by direct synthesis (full black points and black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 6. H_2-TPR patterns of V-HMS samples prepared by impregnation method (A) and by direct synthesis (B).

method exhibit more rapid decrease of the ε_0 value compared to samples prepared by the direct synthesis. This effect indicates more oligomeric units formation or a wider degree of theirs oligomerization compared to samples prepared by the direct synthesis. The values presented in Table 1 indicate that samples with low VO_X concentration contain at first mostly the isolated monomeric T_d units but the relative abundance of these species decreases with the increasing of total vanadium loading. This effect can be clearly seen from Fig. 5 where is displayed the dependence of calculated amount of monomeric species on total vanadium concentration. The amount of monomeric units increases linearly and these species represent significant part of the VO_X species generated on the HMS surface but after reaching *ca.* 4–5 wt.% of vanadium there is reached their maximal concentration and the amount of these units starts to decrease. It is more important that both sets of catalysts exhibit similar maximal concentration of monomeric units and this concentration is reached at the relatively comparable level of vanadium loading.

3.1.4. H_2–TPR and TPO measurements

H_2-TPR curves were measured to determine the scale of dispersion and type of the present active species. The obtained TPR profiles are presented in Fig. 6 and results of their analysis are summarized in Table 1. From the table is visible that samples prepared by the direct synthesis exhibit only one symmetric reduction peak at the temperature about 560–590 °C whereas the samples prepared by the wet impregnation exhibit moreover the shoulder or second reduction peak at the temperature about 640-680 °C. The progressive shift of the major H_2 consumption temperature peak to higher values with increasing amount of vanadium are explained by two ways (i) either this shift can be ascribed to the kinetic or the thermodynamics of the process of VO_X reduction and it is related to the changes in H_2 to surface vanadium ratio or to ratio of (generated $H_2O)/H_2$ during the reduction process with the increasing of vanadium loading [30,42,43] or (ii) due to the gradual formation of polymeric vanadium species [14].

The low temperature peak can be attributed on the basis of our UV–vis spectra and according to literature either to reduction of the solely monomeric highly dispersed VO_X units (type I) [20] or rather to reduction of T_d both the monomeric and the oligomeric $(VO_4^{3-})_n$ species (type II) [44]. The second interpretation is in the
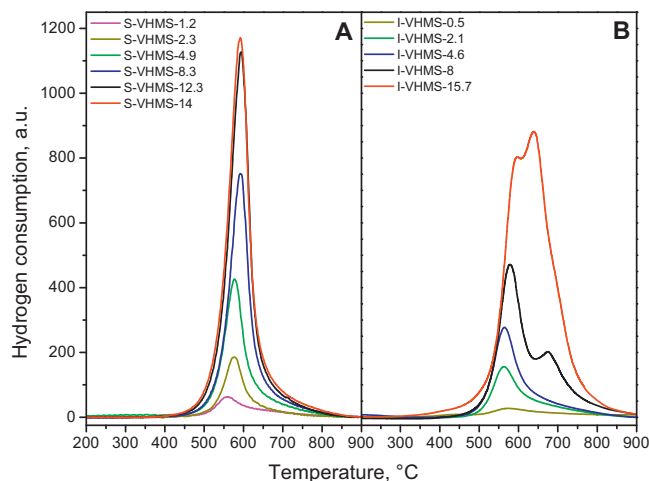
good agreement with the results obtained from our DR UV–vis spectroscopy measurement. The high temperature peak most likely belongs to the reduction of O_h coordinated 2D oligomers and bulk-like 3D V_2O_5 crystallites [14,44]. The presence of V_2O_5 crystallites was clearly proven by XRD results mentioned above.

The overall hydrogen consumption was proportional to the concentration of vanadium and linearly increases with the vanadium loading and corresponds to change of oxidation state of vanadium from the V^V to V^{III}. The changes of oxidation state of vanadium cation are summarized in Table 1. The average $\Delta e/V = 1.95 \pm 0.1$ for impregnated samples corresponds to change of oxidation state of vanadium from the V^V to V^{III}. The samples prepared by the direct synthesis exhibit lower $\Delta e/V$ value 1.75 ± 0.1 and this effect can be ascribed to non-complete extraction of vanadium oxide species from the HMS lattice during the sample pretreatment.

The temperature programmed oxidation experiments were carried out using the sample S-VHMS-4.9 and obtained TPO curves consist of one oxidation peak (not shown here for sake of brevity). The variation of the heating rate β (8, 12 and 20 °C/min) in the TPO causes the changes in position of maximum of this peak to the temperatures 338, 356 and 395 °C. The apparent activation energy of the catalyst reoxidation equal to 44 ± 7 kJ mol^{-1} was calculated using the Kissinger Eq. (3).

3.2. Catalytic tests of n-butane ODH

Both synthesized and impregnated VO_X-HMS catalysts were active and selective in the ODH of *n*-butane with oxygen over the V-HMS catalysts. The reaction products identified in the reaction mixture were: methane (C_1), ethane and ethene (C_2), propane and propene (C_3), 1–butene (1-C_4), *cis*- and *trans*-2-butene (*c*-C_4 and *t*-C_4), 1,3-butadiene (1,3-C_4), carbon oxides (CO and CO_2) and traces of acetaldehyde. The carbon balance was 98 ± 3 % in all the catalytic tests and no maleic-anhydride, other oxygenates or products of significant catalyst coking were not found. The activity of catalysts was stable at least for 10 hours time–on–stream (TOS) and no loss of catalyst activity during the time reported elsewhere [45] was observed. The activity of pure HMS was measured under the same conditions to check reactivity of clear support. It was not observed any activity up to 520 °C. The conversion of *n*-butane only about 3% was detected at 540 °C (for more details see Table 2). This conversion is remarkably lower in comparison to the conversions reached over all tested catalysts. Nevertheless presence of reactions in homogenous phase was proved after initialization by

Table 2
Results of catalytic tests for both sets of catalyst and pure HMS support at 540 °C (m_{cat} = 400 mg, C_4H_{10}/O_2/He = 10/10/80 vol.%, total flow rate of 100 cm^3 min^{-1}).

Catalyst sample name	Conv. (%) C_4H_{10}	Selectivity (%) 1-C_4	c-C_4	t-C_4	1,3-C_4	C_1–C_3 [a]	CO	CO_2	Dehy.[b]	i-Dehy.[b]	1-Butene[c] 2-Butenes	Yield,(%) Dehy.[b]	Productivity[d] Dehy.[b]	TOF (h^{-1})	Ea (kJ mol^{-1})
HMS	3	10	6	2	18	25	22	17	36	37	1.3	1.1	0.04		
S-VHMS-1.2	16	22	9	5	27	11	13	12	63	66	1.6	6.5	0.24	28.9	119
S-VHMS-2.3	29	15	8	4	26	5	17	26	53	63	1.2	10.0	0.38	27.4	91
S-VHMS-4.9	36	14	8	7	21	6	24	20	50	53	1.0	19.7	0.74	27.4	81
S-VHMS-8.3	29	9	5	4	15	3	28	36	33	22	1.0	9.7	0.36	11.9	62
S-VHMS-12.3	27	7	4	2	12	4	34	37	25	21	1.1	6.7	0.25	7.5	39
S-VHMS-14	30	6	4	2	11	6	38	34	22	10	1.0	6.7	0.25	7.4	23
I-VHMS-0.5	6	14	7	4	20	19	20	15	45	40	1.4	1.8	0.07	29.8	116
I-VHMS-2.1	18	10	5	5	16	13	31	20	40	45	1.1	7.1	0.27	28.2	79
I-VHMS-4.6	36	12	6	5	18	9	31	18	42	45	1.0	15.0	0.56	26.9	50
I-VHMS-8	28	7	4	3	13	5	42	25	27	15	1.0	7.6	0.29	11.9	37
I-VHMS-15.7	22	2	1	0	4	2	58	32	8	2	1.0	1.8	0.07	4.8	45

[a] C_1–C_3 is the sum of C_1–C_3 hydrocarbons and acetaldehyde.
[b] Dehy. is the sum of C_4 alkenes, i-Dehy. is the sum of C_4 alkanes at X = 7.5%.
[c] Ratio of 1-butene to (cis-2-butene + trans-2-butene).
[d] Productivity = g_{prod} g_{cat}^{-1} h^{-1}.
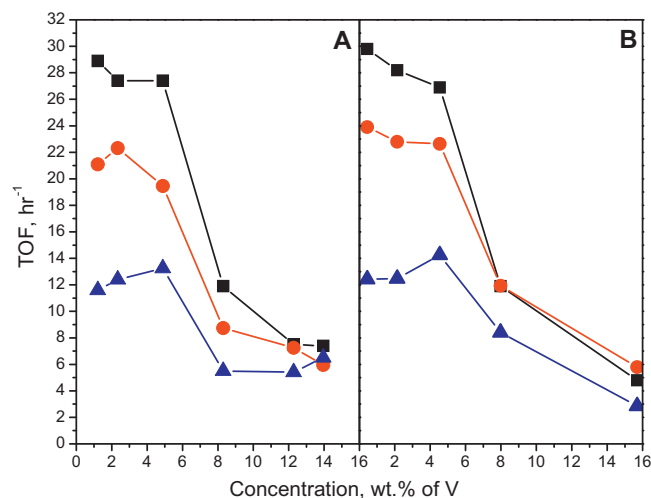

Fig. 7. The activity of synthesized (A) and impregnated (B) V-HMS catalyst in ODH of n-butane expressed by TOF factor at 460 °C (blue triangle and line), 500 °C (red circle and line) and 540 °C (black square and line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

matrix which is in the compliance with previously results published [46].

3.2.1. Catalysts activity in C_4-ODH reaction

The value of turn-over-frequencies (TOF) exhibits similar dependence on the concentration of vanadium for both sets of catalysts as shown in Fig. 7. The all low concentrated samples exhibit approximately constant value of TOF factor (28 h^{-1} for 540 °C) until the vanadium concentration ca. 4.5 wt.% is reached followed by a rapid change of TOF to low value (5–7 h^{-1} for 540 °C). The very similar dependences of TOF vs. V loading were obtained for the all experiments carried out over both sets of catalysts in the temperature range 460–540 °C (see Fig. 7) regardless that at the highest temperature (540 °C) the conversion of oxygen was almost 100% for samples with the high concentration of vanadium.

The vanadium concentration when the TOF starts to decrease corresponds well with the maximal concentration of monomeric VO_X units as it is shown in Fig. 5 or reaching the level 0.7 VO_X per nm^2 for vanadium surface density previously reported [32] as limiting for obtaining the monolayer of monomeric units. Decrease of TOF value clearly evidences that with subsequent increase of vanadium content the significantly less active or non active species in ODH of n–butane are generated and that is why the monomeric VO_X units should be taken as the most active species in the ODH of n-butane.

3.2.2. Selectivity to all C_4-ODH products

The selectivity to products of C_4-ODH remained relatively constant in whole temperature range as it can be seen from Fig. 8. This character of selectivity vs. temperature dependence offers the possibility to compare values of selectivity at the iso-conversion conditions obtained at different temperatures of reaction, however this method is not as rigorous as comparison of iso-conversion data obtained by variation of amount of catalyst used in reaction. The values of selectivity to C_4-olefins obtained for the conversion 7.5% are summarized in Table 2. Similarity of these values with the C_4-ODH selectivity values obtained at 540 °C confirms our assumption of low dependence C_4-ODH selectivity on temperature for our materials under the given reaction conditions. Hence the both sets values can be used for the comparison of selectivity to the C_4-olefins on studied materials.
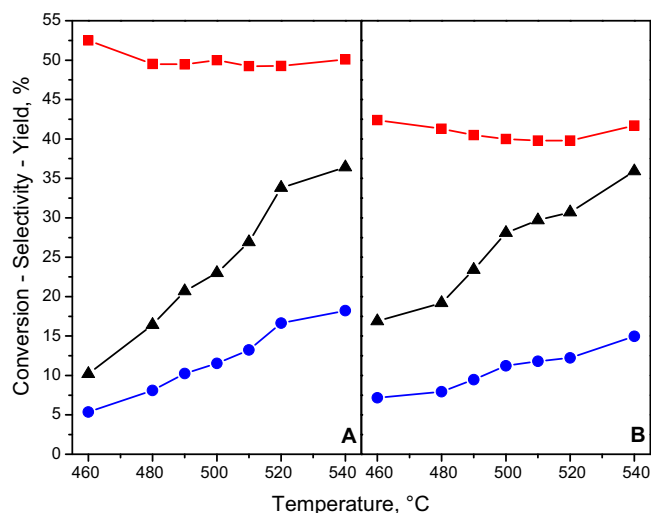
Fig. 8. The conversion (black triangle and line), selectivity (red square and line) and yield (blue circle and line) for representative sample prepared by direct synthesis (S-VHMS-4.9, A) and by wet impregnation method (I-VHMS-4.6, B). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

It can be seen the drop of C_4-olefins selectivity decreases with increasing of the vanadium content from 63% for the sample S-VHMS-1.2 to nearly non-selective catalyst I-VHMS-15.7 with selectivity only about 10% (Table 2). The yield or productivity of C4-ODH products increases with the amount of vanadium until the concentration 4–5 wt.% is reached then these values start to decrease. The maximal yield or productivity obtained was *ca.* 20% or 0.74 g C_4-olefins per gram of catalyst for one hour respectively (S-VHMS-4.9). Similar behaviour was previously published for oxidation of toluene over V-HMS prepared by similar procedure and authors explain this behaviour on the base of different amount of suitable and accessible VO_X species but they didn't propose more detailed specification of these species [47].

This behaviour is probably due to increasing of abundance of oligomeric species with T_d and mainly O_h coordination because these species contain the V–O–V bridging oxygen atoms. According to mechanism introduced by Kung [6] the presence of this type of oxygen allows the formation of alkoxide intermediate which is furthermore oxidized to the products of total oxidation (CO and CO_2).

Although both sets of catalyst exhibit similar trends of conversion on the vanadium loading the selectivity to C_4–olefins is about 10% higher for the synthesized samples than for samples prepared by impregnation method in the whole range of prepared concentrations even for samples with same value of VO_X surface density. Such difference of selectivity to C_4-ODH products can be ascribed to the VO_X species with higher level of polymerization whose are preferentially formed in the samples prepared by the wet impregnation method. These species facilitate consecutive reactions and formation of CO_X. These species cannot be detected on the basis of analysis of VO_X surface density value nor by the analysis of the DR UV–vis spectra with the sufficient accuracy. We can presume on presence of these species on the basis of TPR analysis as it was mentioned above.

3.2.2.1. Selectivity to 1,3-butadiene. When we make analysis of selectivity of individual products of C_4-olefins in detail it can be found out that approximately 40-50% belongs to 1,3-butadiene. The butadiene represents relatively high portion of C_4-ODH products in the whole range of vanadium concentration, temperature and conversion of *n*-butane and oxygen. Similar distribution of C_4-

olefins was published on V-Mg-O materials by Chaar [13] and high selectivity to butadiene was ascribed to basic character of catalysts compared to silica [11,13] as well as to presence of $Mg_3(VO_4)_2$ with isolated tetrahedral species which prohibits deep oxidation [1].

However our observation is in contrast to results published previously on SiO_2 based catalysts. Owens [16] investigated vanadium anchored on amorphous silica and he described only small selectivity to butadiene. More similar results published Liu et al. [14] who studied V-SBA-15 material which exhibited selectivity about 30% (from C_4-olefins only) to butadiene.

The selectivity to dehydrogenation products as well as distribution of C_4-olefins can be related to the acid-base character of the catalysts as it was reported by Blasco et al. [12] on the base FTIR of adsorbed pyridine or Liu et al. [14] on the basis of NH_3-TPD and widely discussed in many other works [1,6,7,10,48]. In our case acid–base character of HMS support (IEP *ca.* 2) extend retention period of reaction intermediates because the olefins (electron-donating molecules with high electron densities at π bonds) are stronger adsorbed on the surface of catalysts then paraffins [1,9,12]. This confirm values of adsorption heats on silanol groups (determined by FTIR spectroscopy) 27 kJ mol^{-1} [49] for *n*-butane and 30–36 kJ mol^{-1} [49,50] for butenes, respectively. The acidity further increases with rising amount of vanadium and it implicates that vanadium species act as an acidic site on silica and that is why we need good distribution of monomeric VO_X species [51].

It seems that more basic character of MgO support predestine this support as the best support for the alkane ODH catalyst but the situation is probably more complicated because according to Albonetti et al. [10] the V/Al/O catalyst exhibit better performance for the ethane ODH than V–Mg–O catalyst. The other effects can control selectivity of ODH reaction and can prevail the influence of acid-base characteristics of support.

On the basis of this fact we can suppose that butadiene originate by direct two-step ODH reaction of the adsorbed hydrocarbon complex over one or more active centers without desorption intermediate to the gas phase. Similar mechanism was recently proposed by Marcu et al. [52] on the basis of TAP measurements over the tetravalent pyrophosphate catalysts. Moreover the large surface area of catalysts facilitates good dispersion and isolation of VO_X species. This has resulted in limiting of deep oxidation of forming intermediates to CO_X.

3.2.2.2. Selectivity to 1-butene and 2-butenes. The ratio of the selectivity of 1-butene to sum of *cis-/trans*-2-butene is 1.5 for samples with lowest concentration of vanadium. When we assume that the first hydrogen abstraction occur on the secondary carbon atom this value corresponds to statistical distribution of products (1-butene: *cis*-2-butene: *trans*-2-butene) 3:1:1 which can be formed by the abstraction of second hydrogen from adjacent methyl and methylene groups. Based on this assumption Chaar et al. [13] attributes this behaviour to fast radical dehydrogenation of adsorbed alkyl intermediate. Similar effect was also observed on other catalytic systems [7,11,45].

This statistical distribution ratio shifts to worth one at highest concentration for both types of samples. This shift is due to unequal participation of 1-butene in consecutive reactions and similar effect was described by Lemonidou [45]. Blasco and Nieto [7] put this shift of distribution of products to the context with acid character of catalysts which probably influences the rate of the consecutive reactions. It is known that 1-butene can isomerize to 2-butene if acid site are present on the catalyst surface [7]. With increasing VO_X loading (IEP of V_2O_5 < SiO_2) increases the acidity of material and that is why the distribution of products shift from statistical distribution of products to thermodynamic equilibrium. We can finally say that distribution of products is predominantly controlled by kinetic effects and not by thermodynamics of process because
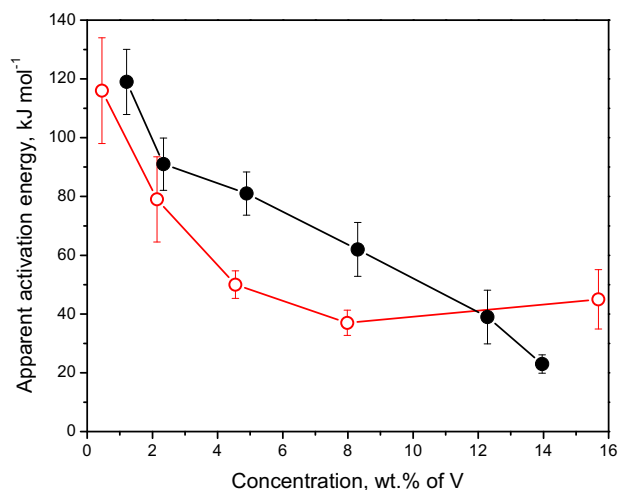
Fig. 9. The apparent activation energy in dependence on the vanadium loading for impregnated (open red points and red line) and for samples prepared by direct synthesis (full black points and black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the thermodynamic control should give the product distribution (1:1:1.1) [7] and no remarkable isomerization of butenes occurs on the surface of catalysts.

3.2.3. Apparent activation energy

The activation energies corresponding to the transformation of n-butane were determined in the temperature range from 460 to 540 °C using conversion data presented in Table 2 according to Arrhenius relationship. The apparent activation energy (E_A) in dependence on the vanadium content is presented in Fig. 9. The value of apparent E_A is about $120 \pm 15\,kJ\,mol^{-1}$ for samples with low concentration of vanadium on the surface and it decreases to $E_A = 40 \pm 8\,kJ\,mol^{-1}$ for higher concentration. It is evident that the change of rate-limiting step in mechanism of ODH n-butane occurs as the vanadium loading increases. The rate-limiting step for low concentration samples is supposed to be the activation of hydrocarbon on the surface by abstraction of hydrogen from secondary carbon [5]. The value $120\,kJ\,mol^{-1}$ is similar to apparent E_A for ODH of n-butane on VO_X–silica ($110\,kJ\,mol^{-1}$ [16]) or on VMgO catalysts ($105\,kJ\,mol^{-1}$ [45]). Because these materials have different textural properties, it can be expected that the apparent activation energy values are most likely affected only by the kinetic of ODH process for our materials as well. Therefore it can be neglected the influence of other processes *i.e.* diffusion to this value.

The value $E_A = 40 \pm 8\,kJ\,mol^{-1}$ for high concentrated samples is close to E_A of reoxidation obtained from the TPO experiments as it was mentioned above. It can be assumed that the reoxidation of active centre is rate-limiting step for samples of high vanadium concentration most likely affected by migration of oxygen atoms through the lattice of VO_X crystallites. We can find vanadium oxospecies with high degree of polymerization over these materials. These centers prefer the total oxidation reactions of n-butane to CO_X and thus the oxygen consumption is high for their reoxidation. This effect is very remarkable especially for samples which contain O_h coordinated vanadium species and that is why the decrease of apparent E_A is steeper for impregnated samples compared to slower decrease of E_A values for samples prepared by direct synthesis.

4. Conclusions

On the basis of this results reported in this paper the following conclusion can be made:

- The isolated monomeric VO_X species play the role of the most active catalytic centre in the ODH of n-butane. The catalytic behaviour of these units is similar for both sets of catalysts regardless of the method of their preparation.
- The amount of isolated monomeric species is comparable for both sets of materials up to total concentration 4–5 wt.% of vanadium but the highest achievable amount of monomeric species was slightly higher for catalysts prepared by direct synthesis.
- The VO_X species with higher degree of polymerization participate in undesired consecutive reactions with ODH products. The direct synthesis method leads to lower extent of formation of these species compared to wet impregnation.
- The method of preparation influences the formation of oligomeric species. The impregnated samples contain higher amount of octahedrally coordinated species compared to samples prepared by direct synthesis.
- The most abundant selective product was 1,3-butadiene with selectivity up to 30%. The total sum of selectivity to all C_4-olefins reached up to 65% over the catalysts prepared by direct synthesis. The samples prepared by wet impregnation exhibit 10% lower selectivity to C_4-olefins compared to catalysts prepared by direct synthesis in the whole range of vanadium concentrations. The selectivity decrease with increasing vanadium content.

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