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Vanadium catalysts
anchored on mesoporous support
in oxidative dehydrogenation of *n*-butane

Annotation of doctoral thesis

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Abstract

The introduced doctoral thesis deals with the study of structural properties and catalytic performance of vanadium oxide containing high surface mesoporous silica materials in oxidative dehydrogenation of *n*-butane (C₄-ODH) to corresponding alkenes. The ODH of *n*-butane could be good alternative to classical dehydrogenation, steam cracking and fluid catalytic cracking processes which have some limitations and they are expected to be insufficient to supply increasing demand for olefins in the coming years.

The main aim of this thesis was investigation of the influence of vanadium oxide species structure and their surface dispersion on silica based materials to catalytic activity in C₄-ODH reaction. Several experimental techniques were used for deep characterization of catalysts. The XRD, SEM and N₂-adsorption were used for the study of textural properties and H₂-TPR, DR UV-vis and Raman spectroscopy for determination of VO_x complex speciation. The most valuable method for determination of vanadium speciation seems to be a new methodology of the measurement and evaluation of DR UV-vis spectra which was developed during this thesis. The suggested methodology utilizes the benefit of the well resolved absorption bands in the UV-vis spectra of samples which were highly diluted by pure silica. By combination of the results obtained from characterization and from measurement of catalytic activity, we can conclude that the highest activity and selectivity to alkenes is reached on materials with high content of isolated monomeric VO_x units with the tetrahedral vanadium-oxygen coordination.

The second aim of this thesis was optimization of catalysts for high catalytic performance in C₄-ODH, which is necessary for potential using in industry. The effect of mesoporous silica support (HMS, SBA-15, SBA-16 and MCM-48) differing in porous structure, the two different method for incorporation of vanadium (the wet impregnation and direct synthesis) and the effect of different titania amount incorporated as support modifier into silica was studied for this purpose.

The best catalytic system seems to be V-SBA-15 catalysts prepared by direct synthesis, which exhibits high butenes productivity (1.9 kg_{prod.}·kg_{cat.}⁻¹·h⁻¹) and sufficient selectivity. If the productivity is used as a criterion of catalytic performance this material belongs to the three best catalytic systems which were reported for C₄-ODH ever.

Keywords: mesoporous silica, DR UV-vis spectroscopy, oxidative dehydrogenation (ODH), vanadium oxide species, butenes

1 Introduction

The continuously growing demand for C₂-C₄ alkenes, which are the building blocks or important intermediates of synthetic rubbers, plastics, automotive fuel components and other valuable chemical products, brings a great challenge for nowadays chemical industry. Currently, the light alkenes are obtained mainly as by products from catalytic or steam cracking of crude oil or natural gas and from fluid catalytic cracking (FCC) of vacuum gas oil. However, present industrial capacity is expected to be insufficient in the coming years, as the demand grows for these important intermediates of the modern petrochemical industry. It stimulates research to improve existing technologies or to develop new ones, which will be able to prepare these materials from cheap and in the future abundant C₂-C₄ alkanes [1, 2]. Alkanes are, not only, cheaper (the current cost of one metric tone of propane is 860 \$/t while the cost of propene 1 105 \$/t (V)) but moreover they have lower impact to environment due to lower toxicity in comparison to alkene or aromatics [3, 4].

Oxidative dehydrogenation (ODH) of *n*-butane could be an alternative to classical used processes. The ODH reaction is thermodynamically favorable and can be carried out at temperature much lower in comparison to a non-oxidative dehydrogenation (practically complete conversion can be attained at temperature about 200 °C lower than those used in dehydrogenation [5]) [6-8]. To a certain extent, the conditions of ODH reaction also 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 lot of consecutive reaction products as described in ref. [1]. Moreover the formed alkenes are approximately four times more reactive then starting butane [8] what causes the decrease of selectivity to desired products with the increasing conversion of butane. Thus the development of suitable catalyst is still unresolved important challenge.

Vanadium oxide based catalysts are very often used as catalysts in ODH reactions. Their application offers several advantages like: (i) lower temperature for the activation of C-H bonds of reactants (limitation of cracking and combustion reactions) and (ii) 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 hydrocarbon molecule. However, in the case of ODH of alkanes, carried out at higher temperatures, the using of bulk vanadium oxides lead to total oxidation products like CO_x. From this reason,

the vanadium oxide is very often deposited on a suitable support in the form of well dispersed VO_x species (vanadium supported catalysts represent 28% of all supported catalysts [9]) [6, 8].

General benefits of the supported catalysts on the mesoporous silica materials are: (i) large surface area which allows a good dispersion of active VO_x species, (ii) relatively high thermal and hydrothermal stability of the support, (iii) good mechanical properties (iii) structure of support (usually micro- or mesoporous) brings advantages in shape selectivity of these materials and last but not least (iv) important point for supported model catalysts is the structural homogeneity of the support material which allows relatively simple characterization and opens the possibility to describe these systems by apparatus of the theoretical chemistry [2, 10, 11].

The support is capable strongly affect the catalytic performance. The textural properties and acid base character of the support are the most important factors [2]. The acid base character influences (i) the dispersion of the vanadium oxide [10] (ii) their structure [10] and (iii) retention period of reactants and reaction intermediates on the surface [4, 10]. From this point of view the MgO support (iso-electric point (IEP) ca. 12.5 [10]) seems as the best support for ODH of alkanes because rising alkenes (more basic than alkanes) are easily desorbed and it suppress consecutive reactions leading to CO_x. Moreover acid character of V₂O₅ (IEP 1.4 [10]) facilitates good dispersion of VO_x species. On the other hand MgO supports have area only about 100-150 m² g⁻¹ what limits attainable vanadium loading [12] and the formation of bulky vanadium-magnesium oxide compounds also occurs on this support [11, 13] what leads to disappearance of the part of vanadium from its catalytic role. From this reason is required to find new support materials with large surface.

The vanadium oxide (VO_x) units supported on the surface of ordered mesoporous silica (SBA-15, HMS etc.) were reported to be potentially suitable catalysts for the ODH of *n*-butane in the past [2, 6, 14, 15]. However, they exhibit relatively low activity and C₄-ODH productivity due to high apparent activation energy of C-H bonds [16]. One possibility how to solve this problem is to prepare a mixed support which combines suitable properties of different supports. A good example could be combination of properties of SiO₂ (high surface area, thermal stability and proper selectivity) and TiO₂ (high activity which allows to carry out the reaction at lower temperatures [6, 17, 18]) in one Si-Ti materials (VII).

VO_x particle might be present at surface of catalysts in four different forms: highly dispersed isolated monomeric units with tetrahedral coordination (group of symmetry T_d or C_{3v}) usually expected to have a structure (support–O)₃V=O (Figure 1 A), one-dimensional oligomeric units connected by V–O–V bonds with distorted tetrahedral coordination (Figure 1 B), two-dimensional polymeric units with a square pyramidal structure (Figure 1 C). At the highest level of VO_x concentration, octahedrally (group O_h) coordinated three-dimensional V₂O₅ crystallites (Figure 1 D) could be generated [6, 8, 9].

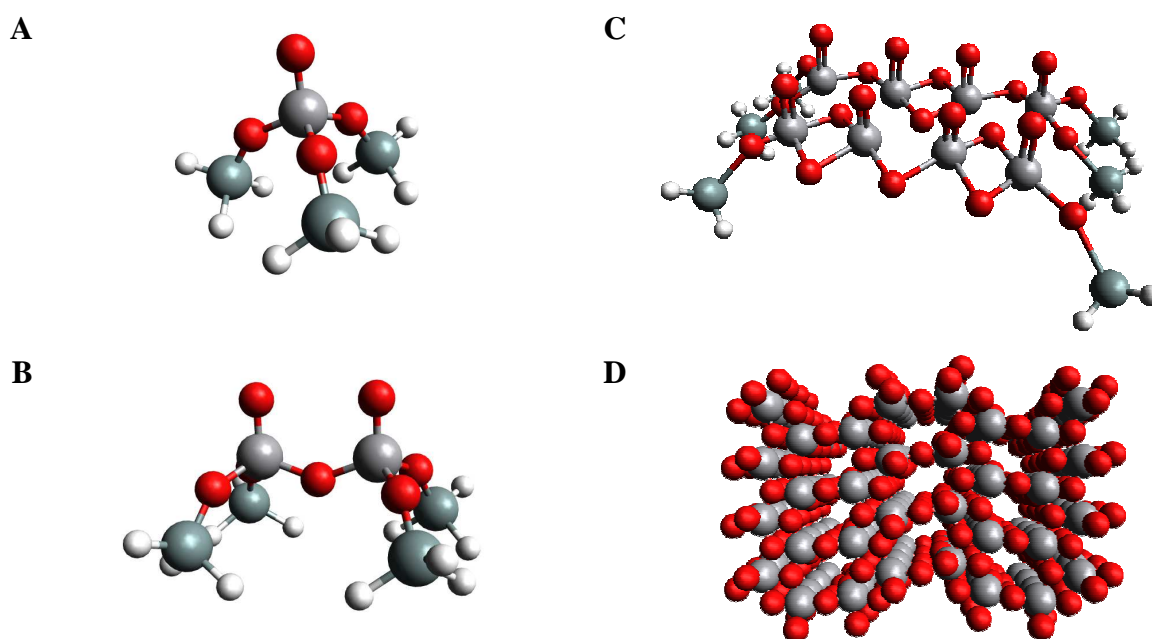


Figure 1 – Possible molecular configurations for supported vanadium oxides (red ball – oxygen, light gray ball – vanadium, dark gray – silicon and white ball – oxygen in support): A) isolated vanadium oxide species with T_d coordination; B) dimeric and 1-D oligomeric vanadium species with T_d coordination; C) 2-D vanadium oxide chains with T_d coordination; D) bulk V₂O₅ crystals with O_h coordination of vanadium atom (IV).

The method of the deposition of active vanadium phase can also strongly influence the nature and abundance of rising VO_x species. The simple wet impregnation method of vanadium salt (NH₄VO₃, vanadyl sulphate, vanadyl acetylacetonate) is very often used for the deposition of VO_x species [14, 19-22]. 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 vanado-silicate 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. In

this case, the vanadium species are incorporated directly to mesoporous structure, where the VO₄ units with tetrahedral coordination substitute the SiO₄ isomorphly [23-25].

2 Aims of the study

This doctoral thesis deals with supported vanadium catalysts on mesoporous materials which are characterized by broad range of analytical techniques and tested in C₄-ODH reaction. The two main aims of this doctoral thesis are:

- (A) Investigation of the influence of vanadium oxide species structure and their surface dispersion on silica based materials to catalytic activity in ODH of *n*-butane.
- (B) Optimization of these materials for high catalytic performance in ODH, which is necessary for potential using in industrial plants.

To achieve these two main objectives is necessary to answer some partial question:

- (i) How to distinguish and quantify vanadium oxide species in the VO_x-silica catalysts?
- (ii) Which VO_x species are the most active in *n*-butane ODH?
- (iii) Is it possible to influence VO_x speciation and catalytic activity by way of used preparation?
- (iv) Could be the dispersion of VO_x species and performance of catalysts influenced by textural structure of used support?
- (v) How the support chemical composition affects the VO_x dispersion and catalytic activity?

3 Experimental

Because the experimental setup and conditions are in detail described in Paper I-VII related to this doctoral thesis, only basic description of preparation and characterization of catalysts will be given in following paragraphs.

3.1 Preparation of catalysts

The silica supports were prepared at ambient conditions or by hydrothermal treatment. The tetraethylorthosilicate (TEOS, Aldrich) was used as a silica precursor in all cases (I-VII) and tetraethylorthotitanate (TEOT, Aldrich) was used as a titanium source in the case of Ti-HMS preparation (VII). The structure directing agent (SDA) was chosen

according to the required structure (V). The template was removed from the structure of mesopores by calcination in a stream of air at 540 °C for 8 hours with heating rate 1 °C min⁻¹ in all cases.

Investigated vanadium catalysts were prepared in two ways (i) by impregnation and (ii) by direct synthesis. In the first case, vanadium oxo-species was introduced onto the silica support by the wet impregnation from EtOH solution of vanadyl acetylacetonate (VO(acac)₂) (I-V, VII). The procedure for the preparation of supported vanadium catalysts by direct synthesis method was almost the same as procedure of support preparation but in the first step of synthesis the source of vanadium (VO(acac)₂ (I-II, IV), NH₄VO₃ (VI)) were added directly to the homogeneous solution. The calcination of samples was carried out at 600 °C in air stream for 8 hours.

3.2 Catalysts characterization

The vanadium content in all investigated samples was determined by X-ray fluorescence spectroscopy by ElvaX (Elvatech, Ukraine) equipped with Pd anode. Another details you can find in our papers (IV-V).

The structure and crystallinity of catalysts were usually probed by scanning electron microscopy (SEM) (V, VII) using JSM-5500LV microscope (JEOL, Japan) and by X-ray diffraction (IV-V, VII) (D8-advance diffractometer, Bruker AXE, Germany) in the 2 θ range of 2–35° with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$)

Specific surface area and textural properties of investigated catalysts were measured by means of nitrogen adsorption/desorption at temperature of liquid nitrogen for verification of mesoporous structure by using ASAP 2020 equipment (Micromeritics, USA). Prior to adsorption isotherm measurement, the samples were degassed at 300 °C under turbo molecular pump vacuum for 8 h. Additional details are given in paper (V, VII) and in Ref. [22].

Distribution and coordination of vanadium species was investigated by UV–vis diffuse reflectance and Raman spectroscopy. DR UV–vis spectra were measured under dehydration conditions (independently checked on selected samples by UV–vis–NIR spectroscopy monitoring vibrations of OH overtones) at granulated (0.25–0.50 mm) materials by GBS CINTRA 303 spectrometer (GBC Scientific Equipment, Australia) equipped with a Spectralon coated integrating sphere using a Spectralon coated discs as a standard. The spectra were recorded in the range of the wavelength 190–850 nm. The absorption intensity was expressed using the Schuster–Kubelka–Munk equation

$F(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$, where R_∞ is the diffuse reflectance from a semi-infinite layer (I-III). Raman spectra were also measured under dehydrated and fully oxidized state of catalysts (dehydration and oxidation protocol was the same as for DR UV-vis measurement and more details are given in Paper (III)) by a Labram HR spectrometer (Horiba Jobin-Yvon) in the case of spectra excited by 514.5 nm line of an Ar⁺/Kr⁺ laser. UV Raman spectra were measured using Micro-Raman Renishaw RM 1000 spectrometer. Spectra were excited by 325 nm HeCd laser (III, V).

Redox behaviour of VO_x surface species was investigated by temperature programmed reduction by hydrogen (H₂-TPR) using the AutoChem 2920 (Micromeritics, USA). Usually, the sample was oxidized in oxygen flow before reduction. The reduction was carried out from 100 °C to 900 °C in flow of reducing gas (5 vol.% H₂ in Ar). The changes in hydrogen concentration were monitored on TCD detector. For more details you can see experimental part of our papers (I, IV, V, VII).

In addition to these most used method a few others was used in some special cases. For verification of successful incorporation of titanium to the HMS matrix was used FT-IR spectroscopy (VII), thermal stability of samples was investigated by TG-DTA (VII) and apparent reoxidation activation energy E_A was studied by O₂-TPO (IV).

3.3 Catalytic tests in ODH reaction

The *n*-butane oxidative dehydrogenation (C₄-ODH) reaction was carried out using a plug-flow fixed-bed reactor at atmospheric pressure in the kinetic region and at the steady state conditions of the reaction. Usually, the activity and selectivity of catalysts were tested at 540 °C in the dependence on contact time due to possibility compare the catalysts at iso-conversion conditions. The feed composition was usually C₄H₁₀/O₂/He = 10/10/80 vol.% (IV, VII) or 5/5/90 vol.% (V, VI) with a total flow 100 cm³min⁻¹ STP. The analysis of reaction mixture composition was made by on-line gas chromatograph equipped with TCD and FID detectors. The feed conversion, selectivity to products, productivity and turn-over-frequency (TOF) were calculated based using Eq. 4-6 (IV).

4 Results and discussion

4.1 Characterization of VO_x species

The supported vanadium oxide catalysts are very complex materials and the determination of the detailed speciation of vanadium oxide species present on the surface

of the support materials is still challenging task in the process of the catalyst characterization because the knowledge of the prevailing molecular structure of surface vanadium species is an essential task for understanding the structure – catalytic activity relationship. The presence of the various structures of the supported vanadium phase has been extensively characterized by different techniques, especially by spectroscopic techniques (FT-IR, Raman, XANES/EXAFS, DR UV-vis, solid-state MAS ^{51}V NMR, ESR, EPR, SEM, TEM etc.).

Characterization by DR UV-vis, Raman and H_2 -TPR was used as the main technique for study of VO_x dispersion and oxidation state in this thesis. However, a few problems had to be solved before their application for study of our catalysts (I-III).

4.1.1 DR UV-vis spectroscopy

Characterization by DR UV-vis spectroscopy is frequently used because it is widespread, relatively cheap, and a simple experimental technique which can provide information about the different oxidation states and local coordination geometry of supported vanadium oxide species.

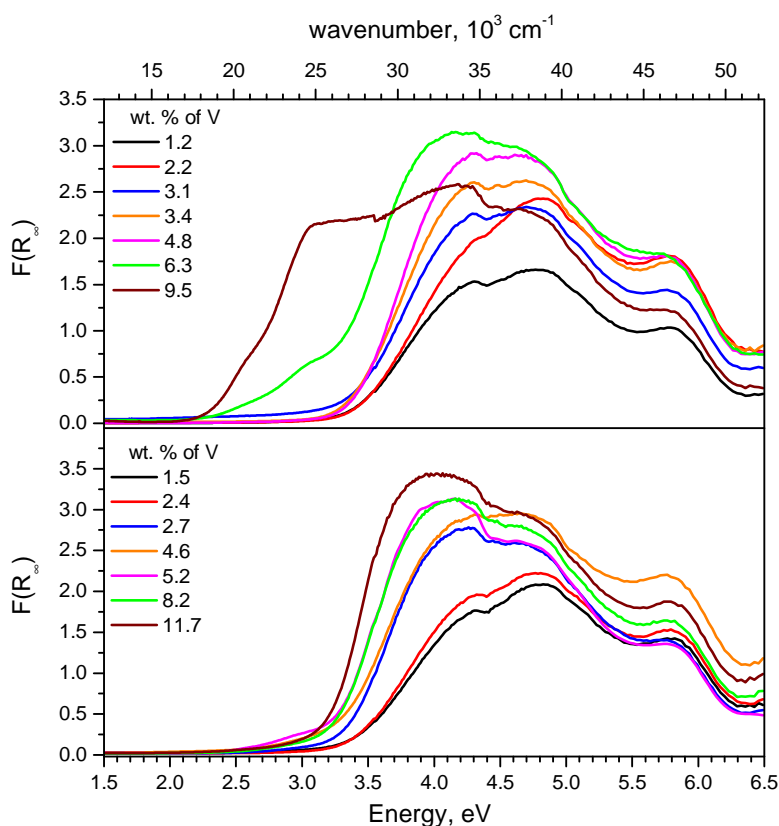


Figure 2 – Spectra of dehydrated V-HMS (impregnated – top and synthesized – below) samples without dilution (II).

The DR UV–vis spectra measured in the range 1.46–6.5 eV (850–190 nm) of dehydrated V-HMS materials are presented in the Figure 2 or two sets of samples, which were prepared by direct synthesis or by wet impregnation, respectively (II, IV). These spectra consist of several ligand to metal charge transfer (LMCT) absorption bands characteristic for samples containing vanadium oxide species supported on siliceous. The d-d absorption bands characteristic for the V^{+IV} in the region 1.55-2.07 eV were not observed in the obtained spectra. This fact confirms that all vanadium atoms are in oxidation state (+V).

However, the measured DR UV–vis spectra usually consist of broad, absorption bands which are overlapped with each other and moreover these spectra is not proportional to amount of vanadium concentration (Figure 3 B). These facts complicate detailed speciation of vanadium oxide species present on the surface of the support and that is why many contradictory interpretations appear very often in published papers (II). This fact was reported already in the past by Catana at al. [26] and completely prohibits the quantitative or semi-quantitative analysis of spectra.

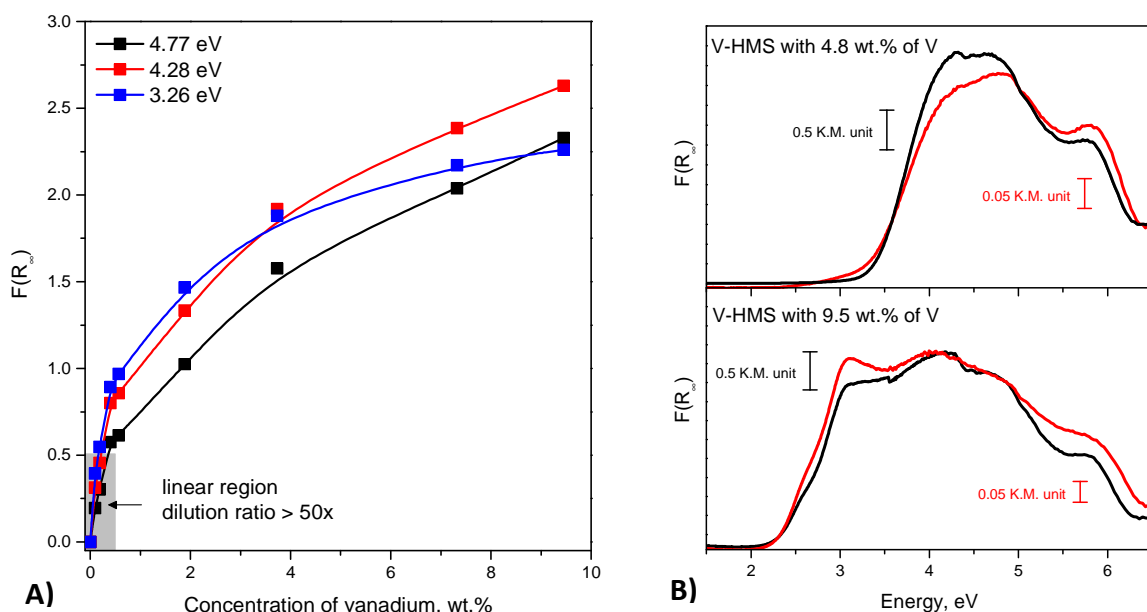


Figure 3 – A) Dependence of spectral intensity for subsequently diluted V-HMS (concentration of vanadium is related to the resulting mixture) (II).

B) Comparison of spectra of pure (black line) and 100 times diluted (red line) samples (II).

Gao [27] partly eliminated this hindrance by using of methodology based on the evaluation of absorption energy edge (ϵ_0) from UV–vis spectra using the expression introduced by Tauc [28] in the form: $(F(R_\infty) \cdot h\nu)^2 = (h\nu - \epsilon_0)$, where the ϵ_0 - the energy

edge values were determined from obtained plots. However, this method is inapplicable for samples containing the remarkable amount of octahedrally coordinated species (the sample with high concentration of vanadium and absorption bands in the region 2–3 eV (II) [21]). Moreover the determination of the ϵ_0 value is rather subjective as well the wrong baseline correction can limit the applicability of this methodology (I, II).

The comparison of the spectra of the pure and diluted samples V-HMS-4.8 and V-HMS-9.5 displayed at Figure 3 B presents the retained width of these spectra. This fact demonstrates that vanadium oxide species supported in porous material has no tendency to redistribute itself to diluting agent as it can occur in the case of material supported on the external surface of nonporous SiO₂ based supports. Moreover, values of the integral area of diluted spectra are approximately proportional to the concentration of vanadium in V-HMS samples (II).

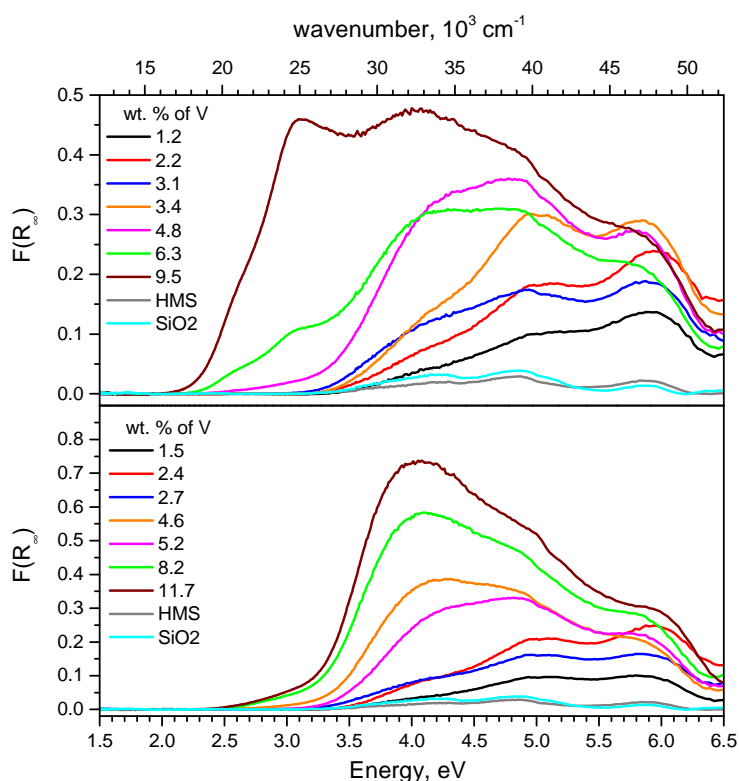


Figure 4 – Spectra of diluted V-HMS (impregnated – top and synthesized – below) materials with dilution ratio to pure silica 1:100 (II).

The Figure 4 shows DR UV-vis spectra of V-HMS samples diluted by amorphous silica with the constant ratio 1:100. Such obtained spectra exhibit more clearly separated bands which offer the possibility to attribute observed absorption band to individual VO_x units more reliably. On the basis of our methodology described in detail in Paper II, we

deconvoluted spectra of diluted samples into five different UV–vis bands denoted as A–E. [Figure 5](#) presents the comparison of the experimental spectra with the model curves for the four selected samples.

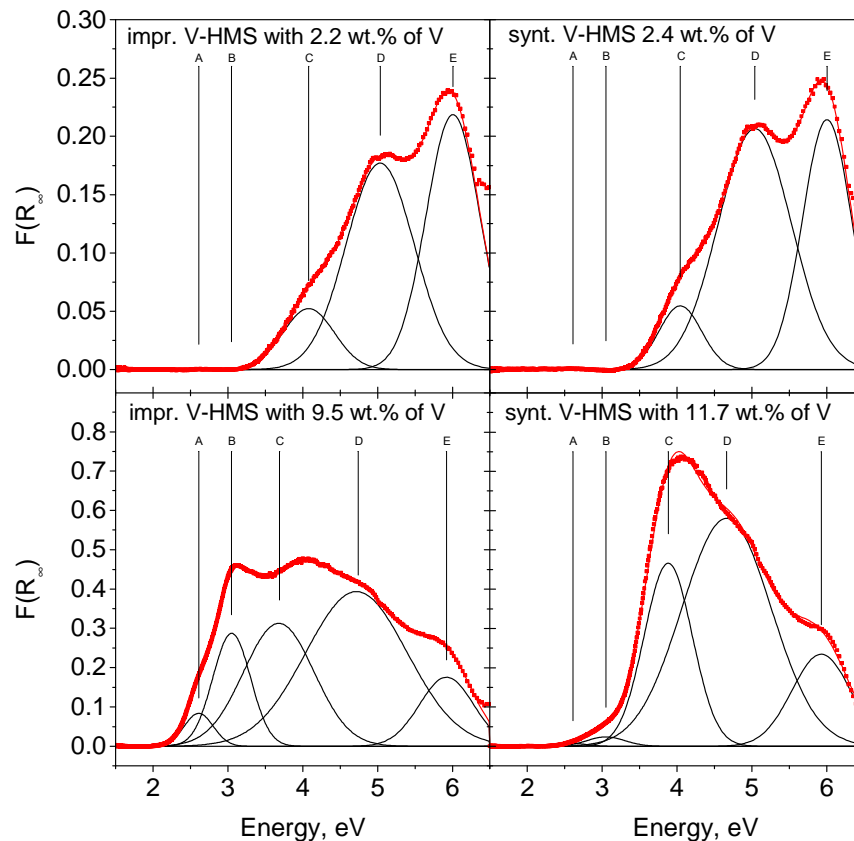


Figure 5 – Results of the deconvolution of experimental spectra by method described in Paper II. Red points are experimental data, the red line is the fitted envelope curve, and black lines are individual spectral bands.

Highly concentrated samples prepared by the wet impregnation exhibit intensive absorption bands at the region 2.5–3.5 eV. The absorption bands can be clearly ascribed to the presence of O_h coordinated bulk-like VO_x because only the V_2O_5 with the edge of absorption energy 2.26 eV has absorption bands in this region (I, II). All diluted V-HMS samples have in the range 3.8–6.5 eV three absorption bands at positions 4.0, 5.0, and 5.9 eV. Clearly separated absorption bands offer the possibility to more reliably attribute observed absorption band to either T_d monomeric or T_d oligomeric units. It was done on the base of comparison spectra of samples with spectra of referent materials (Na_3VO_4 as representative of compound composed from pure T_d monomers and $NaVO_3$ as source of T_d oligomeric units) (II). The band with maxima position approximately at 4 eV can be attributed to T_d oligomeric species. The band at ca. 5.9 eV belongs to T_d monomeric

species and the band with maximum at approximately 5 eV is linear combination of both T_d monomeric and T_d oligomeric species, respectively. Assignment of individual bands in UV-vis spectrum is for better illustration shows in Figure 6.

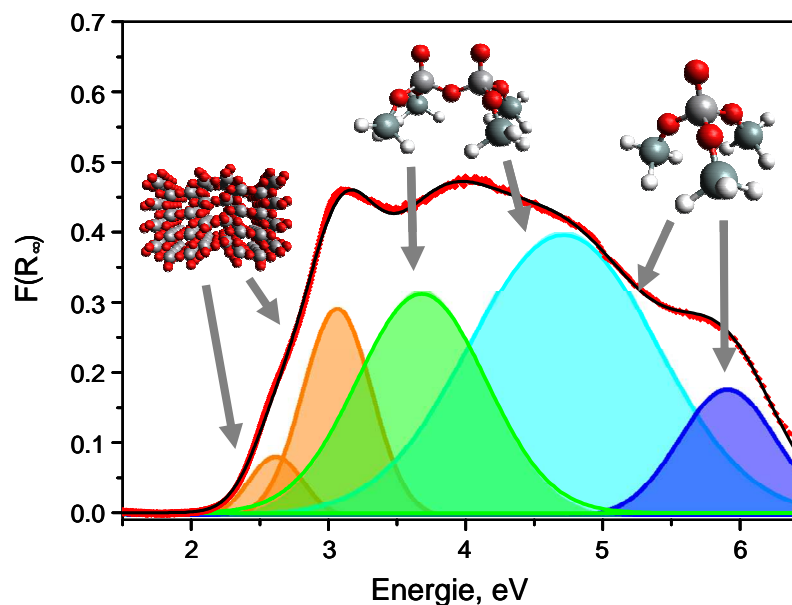


Figure 6 – Assignment of individual bands in UV-vis spectrum to individual VO_x species for V-HMS sample with 9.5 wt.% of V.

4.1.2 Temperature programmed reduction by hydrogen

Temperature programmed reduction by hydrogen (H_2 -TPR) is next frequently used technique for characterization of supported metal oxide. This technique has close relation to redox properties of VO_x species under real catalytic conditions. TPR further indicates whether the vanadium species are accessible for a redox process which is an important proof of successful synthesis of sample because during the preparation by direct synthesis some part of vanadium could be buried deep in silica walls (IV) [22, 29]. Nevertheless reliable assignment of individual peaks in TPR profiles to particular species is not solved yet (I).

The TPR profiles reported in literature [19, 22, 30] exhibited one, two or sometimes even three reduction peaks with temperature maximum ranged usually from 560 to 700 °C. The low temperature peak is usually attributed to the reduction of the isolated monomeric units whereas the high temperature peak is attributed to reduction of oligomeric units and peak with temperature maximum about 700 °C is ascribed as proof of V_2O_5 bulk-like species presence. Nevertheless this assignment does not agree with results from the

UV–vis spectroscopy as it is evident from UV–vis spectra and TPR profiles comparison in our papers (I, IV-V, VII) or in Ref. [22, 30].

On the base of deeper investigation of H₂-TPR and UV–vis spectra (I, IV) was suggested new interpretation of individual bands in TPR profiles which is in good agreement with results obtained by DR UV–vis measurement. The Figure 7 shows representative UV–vis spectra and TPR profiles of V-SBA-15 materials with different population of vanadium species. The first peak in the TPR profiles of vanadium oxide supported on silica materials can be definitely assigned to the reduction of all unit with T_d coordination (monomeric and oligomeric) and the second peak pertains to the vanadium species with O_h coordination (2D and 3D oligomers). The third peak with very sharp maximum could be ascribed to large bulk-vanadium V₂O₅ crystallites with O_h-coordination. Our claim is in a good agreement with interpretation suggested by Arena at al. [30].

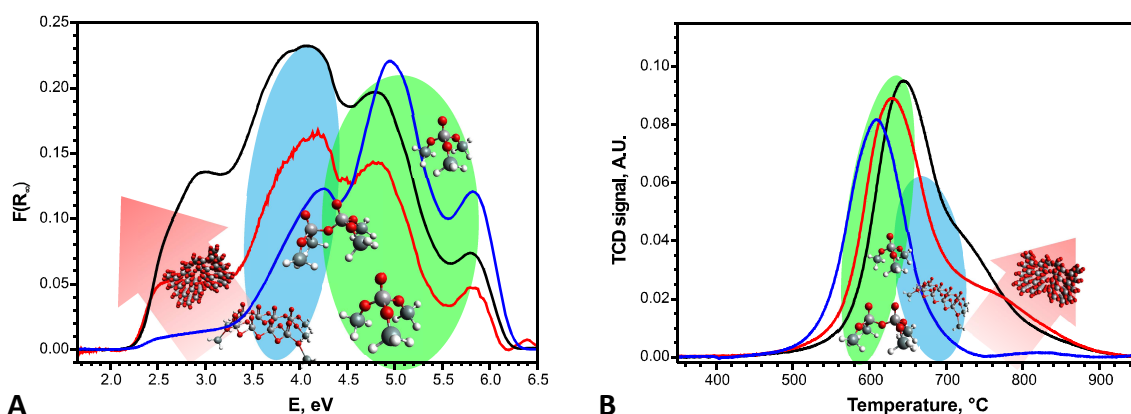


Figure 7 – A) DR UV-vis spectra and B) H₂-TPR profiles of V-*SBA-15* samples prepared by direct synthesis with different population of individual VO_x species.

4.1.3 Raman spectroscopy

Raman spectroscopy is also very often used for characterization of supported vanadium catalysts. However, the using of Raman spectroscopy for VO_x/SiO₂ characterization has some problems and restriction. Firstly, the structure information relies on a correct assignment of the observed bands to vibrational modes. The main problem for VO_x/SiO₂ materials is the strong vibrational coupling between the vanadia species and the silica support [31, 32]. These vibrations cannot be separated by an easy way and hence it may be impossible to assign each of the Raman bands to a single specific bond vibration (III, V).

The second fundamental problem is the fact that Raman spectra (shape, intensity) depend on laser wavelength which is used for excitation of Raman spectra. Evidently, visible Raman spectrum is totally different from ultraviolet Raman spectrum (see [Figure 8](#) and [Figure 9](#)). This is due to the fact that different excitation wavelengths could be absorbed by different vanadium species in the sample and therefore different resonance enhancement effect control of Raman band intensities can occur (III). For deeper investigation of this statement, we compared visible and UV Raman spectra of samples with various distributions of vanadium complexes on the silica support (see [Figure 9](#)) with results obtained from analysis of DR UV–vis spectra (III).

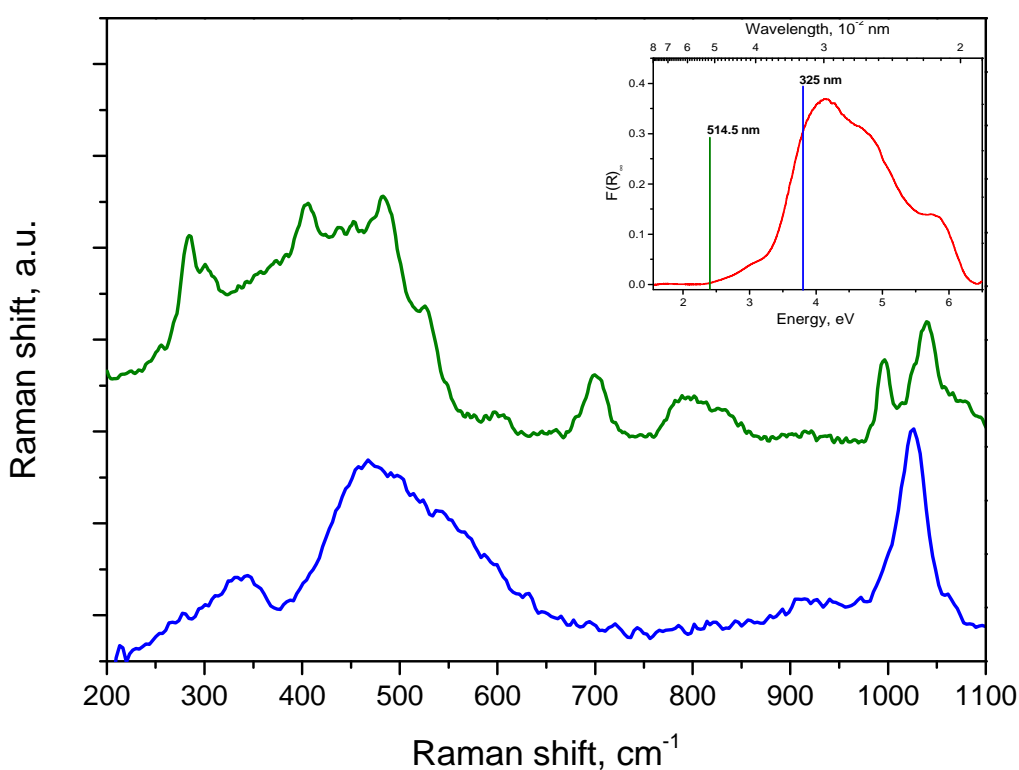


Figure 8 – Raman spectra of dehydrated V-HMS with 6 wt.% of V at 514.5 nm (green line) and 325 nm (blue line) excitation. Inset: DR UV–vis spectrum of the same sample with marked position of lights of individual lasers used for excitation of Raman spectra.

The green laser (514–532 nm) is one of the most frequently used excitation laser and in this case the resonance of V_2O_5 could be occurring very easily. This is the reason that most of the visible Raman spectra contain mainly very intensive signals belonging to crystalline V_2O_5 (set bands at 282, 301, 404, 520, 697 and 993 cm^{-1}). Bands belong to other vanadium species are very broad with low intensity (except band *ca.* 1 035 cm^{-1}) and hence they can not be used for detailed description of vanadium speciation (V).

Band at $1\ 035\ \text{cm}^{-1}$ is usually assigned to terminal V=O stretching vibration. Shift of this vibration band to higher wavenumbers was frequently taken as proofs of changes in the extent of polymerization of VO_x species on supports like Al_2O_3 , ZrO_2 , TiO_2 etc. However, no shift of this Raman band was observed in the case of VO_x supported on silica. Hence some authors predict presence only monomeric VO_4 and/or microcrystalline V_2O_5 species on the silica surface [33, 34].

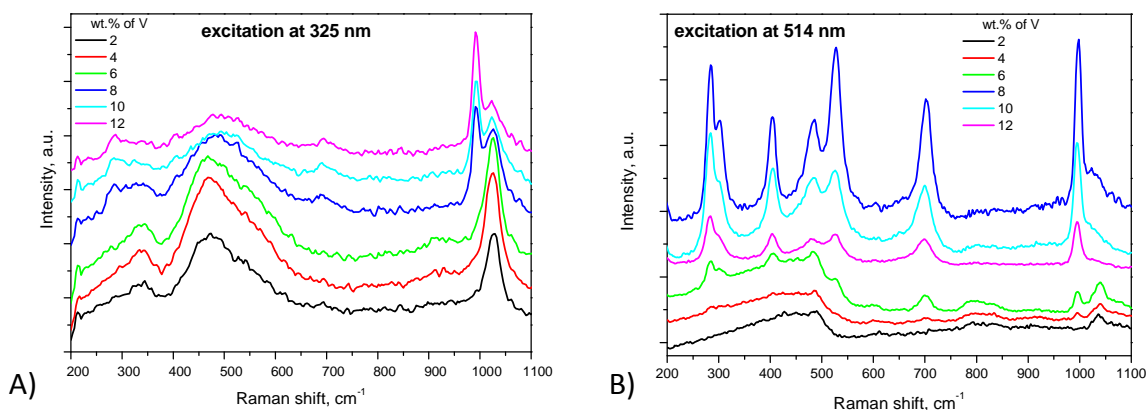


Figure 9 – Visible (A) and UV (B) Raman spectra of dehydrated impregnated V-HMS samples with different concentration and VO_x units population.

However, this interpretation is in contradiction with our results obtained from detailed analysis of DR UV–vis spectra and with conclusions reported in literature as well [35–37]. We prove that changes in population of oligomeric and monomeric VO_x species (determined on the basis of DR UV–vis spectra decomposition (II, III)) in individual samples are not manifested by significant changes in the character of Raman signals (Figure 9). From this data, it is clear that interpretation of Raman spectra is complicated and using of Raman spectroscopy for characterization of VO_x species on silica surface is rather problematic and it could lead to misinterpretation which has been published previously by Dobler [38] as well. On the other hand, Raman spectroscopy is very sensitive technique (mainly at excitation by 514 nm laser) for monitoring of microcrystalline V_2O_5 species even in low concentration, which could not be detected by DR UV–vis or XRD (III).

4.2 Catalytic activity in C_4 -ODH

The main reaction products identified in the reaction mixture were: methane, ethane and ethene, propane and propene, 1-butene, *cis*- and *trans*-2-butene, 1,3-butadiene and carbon oxides (CO and CO_2). The carbon balance was $98 \pm 3\%$ in all the catalytic tests and

oxygenates or products of coking were not found. The activity of catalysts was stable at least for 10 hours time-on-stream (TOS) (IV, V, VII) and no loss of catalyst activity during the time reported elsewhere [13] was observed. The conversion of bare matrix or empty reactor was negligible in comparison with vanadium catalysts.

4.2.1 Activity of the individual vanadium species in ODH of *n*-butane

The role of individual VO_x species in C₄-ODH was investigated on two sets (synthesized and impregnated samples) of V-HMS catalysts differing in amount and distribution of VO_x species. The population of individual VO_x species was determined on the base of energy edge evaluation from UV-vis spectra evaluation (IV) or by mathematical deconvolution of UV-vis spectra of diluted samples (V). The relative amount of oligomeric T_d coordinated units very well corresponds to both, catalytic activity (expressed like apparent TOF) and selectivity to desired C₄-deh. products, respectively (see Figure 10). The all low concentrated samples exhibit approximately constant value of TOF factor (28 h⁻¹ at 540 °C) until the vanadium concentration ca. 4–5 wt.% is reached followed by a rapid decrease of TOF value (5–7 h⁻¹ at 540 °C). Decrease of TOF value clearly evidences that with subsequent increasing of vanadium content the significantly less active or non active species in ODH of *n*-butane are generated.

No only activity, but also selectivity to C₄-deh. products rapidly decrease. This behaviour is probably due to increasing of abundance oligomeric species with T_d and mainly O_h coordination because these species contain the V–O–V bridging oxygen atoms which are readily available for reaction. According to mechanism introduced by Kung [8] the presence of this oxygen allows the formation of the products of total oxidation (CO_x).

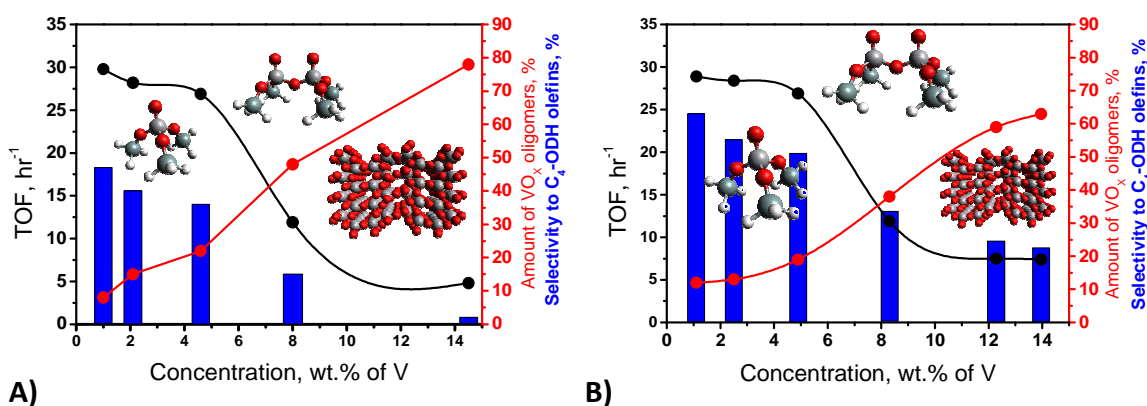


Figure 10 – The relative amount of T_d oligomers (red line) as function of vanadium concentration and its impact on activity (black line) and selectivity (blue bars) for samples prepared by wet impregnation (A) and direct synthesis (B). Data originated from Paper IV.

Finally, we can conclude that the isolated monomeric VO_x species play the role of the most performance catalytic centre in the ODH of *n*-butane, because monomeric units are much more active and selective than all other vanadium oxide species which we can found on silica support.

4.2.2 Catalytic activity – influence of support structure and method of VO_x species deposition

Despite the fact, that there are many different structures of silica [39] only the SBA-15 and amorphous silica was investigated in ODH of *n*-butane. Nevertheless, as shown by the results obtained in ODH of propane, the type of support can affect the performance of catalysts [40, 41]. However, it must be noted, that differences were not significant. More significant differences in the catalytic behaviour could be expected in the case of *n*-butane ODH due to higher sensitivity of this reaction to the individual structure of VO_x species (IV). Therefore, we report comparison of catalytic performance of vanadium containing siliceous with high surface and different structure (HMS, SBA-15, SBA-16 and MCM-48) (V).

It was observed that in addition to the channel structures (1D - 3D) materials differ mainly in the relative abundance of monomeric T_d-coordinated units. The highest relative abundance of these units (determined from deconvoluted UV–vis spectra) can be found on the SBA-15 support (approximately about 82 % relative amount for sample with 3.6 wt.% of vanadium). We can sort tested materials, on the basis of the supports tendency to generate the monomeric species, in the following order HMS < SBA-16 ≈ MCM-48 < SBA-15 (V). More details about physicochemical properties are in Table 1.

High capacity of monomeric species on SBA-15 can be given by the fact that SBA-15 silica represents mesoporous material with regular, very well defined porous system characterized by relatively higher volume of mesopores [42]. Hence, the vanadium source in solvent solution can easily penetrate to the porous system from outer medium and spread homogenously on the silica wall. In this case the overconcentration in microspores does not occur contrary to worm-like (HMS) or ink-bottle (MCM-48) structure with weaker regularity and larger amount of micropores (V).

Previous paragraph shows that the incorporation of vanadium by impregnation may cause creation of large amount of oligomeric species (in the areas of solution accumulation) in less defined structures. This problem could be solved by using of the different method of vanadium incorporation. The direct synthesis of vanadium silicate in

one step is often denoted as the best method for preparation of supported catalysts [22, 24, 25] and that is why we report comparative study of two sets of V-HMS differing in amount and distribution of VO_x species (IV). The samples with the vanadium concentration less than approximately 4–5 wt.% of V exhibit nearly the same amount of monomeric units and these species represent significant part of the VO_x species generated on the surface but the highest achievable amount of monomeric species was slightly higher for catalysts prepared by direct synthesis (see Figure 10). The oligomeric and polymeric units with wider degree of oligomerization, which are formed in higher extent in the samples prepared by the wet impregnation method, start to generate after reaching ca. 4–5 wt.% of V (II, IV). Above this concentration polymeric VO_x species with high polymerization degree and bulk like V₂O₅ are generated in the case of impregnated samples and it means rapid loss in activity and selectivity to alkenes (IV). The relative amount of oligomeric species in both sets of samples and their relationship to catalytic activity is presented in Figure 10.

Table 1 - Physico-chemical characterization and main catalytic results at iso-conversion of *n*-butane 13% for different V-containing high-surface mesoporous siliceous materials (V).

sample	V ^a , wt.%	S _{BET} , m ² g ⁻¹	V _{MI} ^b , cm ³ g ⁻¹	V _{ME} ^c , cm ³ g ⁻¹	D _{ME} ^d , nm	X _{mono} ^e	X _{oligo} ^e	X _{Oh} ^e	S _{TDS} ^f , %	P _{TDS} ^g ,	TOF h ⁻¹
HMS		879	0.010	0.189	6.9						
SBA-15		780	0.060	0.820	6.7						
SBA-16		710	0.073	0.510	3.9						
MCM-48		820	0.068	0.770	7.0						
V-HMS	3.6	640	0.025	0.176	7.1	0.42	0.58	0	53	0.32	16
V-SBA-15	3.6	600	0.030	0.730	5.6	0.82	0.18	0	58	0.57	26
V-SBA-16	3.6	570	0.043	0.309	4.0	0.56	0.44	0	58	0.41	19
V-MCM-48	3.6	670	0.045	0.678	6.0	0.55	0.45	0	43	0.31	19

^a vanadium content determined by XRF method

^b V_{MI} micropore volume determined by using the t-plot method

^c V_{ME} mesopore volume determined by Barret-Joyner-Halenda (BJH) algorithm

^d D_{ME} mesopore diameter determined by BJH algorithm

^e relative amount of T_d-monomeric, T_d-oligomeric and O_h units

^f S_{TDS} = selectivity to all C_{4-deh.} products

^g P_{TDS} = productivity to all C_{4-deh.} products $\frac{\text{g}_{\text{prod}}}{\text{g}_{\text{cat}} \cdot \text{hr}}^{-1}$

Based on our results (IV, V) we can suggest that the most promising catalytic system for ODH of *n*-butane could be V-SBA-15 prepared by direct synthesis. In the Paper VI we report simple one-pot synthesis of V-SBA-15 catalyst according procedure reported by Gao et al. [31] and its high catalytic performance in ODH of *n*-butane.

Directly synthesized V-SBA-15 catalysts with 6.5 wt.% of vanadium shows significantly higher TOF value (45 h^{-1}) in comparison with previously published TOF value for V-SBA-15 system prepared by impregnation ($22\text{-}35 \text{ h}^{-1}$) (V) [14, 43]. Not only high activity, but also relatively high value of selectivity to desired products ($S_{\text{C}_4\text{-deh}} = 59 \%$ at 13 % of *n*-butane conversion), which was equal to selectivity achieved over impregnated V-SBA-15 with 3.6 wt.% of V (see Table 1). The big advantage of samples prepared by direct synthesis is the fact that the high selectivity value could be obtained even over samples with the high vanadium concentration in comparison with samples prepared by impregnation (IV, V).

The catalytic productivity (P) is generally accepted like the best criterion for comparison of different catalytic systems tested in one reaction but under different conditions and it is also one of evaluation criteria for potential industrial using (the lowest limit for industrial using is $1 \text{ kg}_{\text{prod.}} \text{ kg}_{\text{cat.}}^{-1} \text{ h}^{-1}$ [44]). The productivity value obtained over our synthesized V-SBA-15 catalyst ($1.9 \text{ kg}_{\text{prod.}} \text{ kg}_{\text{cat.}}^{-1} \text{ h}^{-1}$) is one of three highest $\text{C}_4\text{-deh}$ productivity values which were published for ODH of *n*-butane in literature (VI) [45, 46].

4.2.3 Activity of catalyst influenced by support compositions – Ti-HMS

The main restriction of vanadium oxide catalysts supported on silica is low monolayer capacity of VO_x species, which is only 0.7 VO_x per nm^2 [47]. However, this disadvantage is compensated by large specific surface area of mesoporous silica materials. The second problem is low activity of vanado-silicates due to relatively high apparent activation energies of C–H bond over VO_x supported on SiO_2 [16, 48].

This problem could be solved by using of VO_x species supported on TiO_2 (anatase). These catalysts showed the highest activities in ODH reactions and moreover they allow carry out the reaction at lower temperature [6, 16]. Nevertheless, VO_x anchored on TiO_2 support has relatively low selectivity in ODH reaction and low specific surface area, which can be further reduced by sintering during the thermal treatments. This property precludes the application of TiO_2 as conventional support for ODH catalysts (IV, VII).

This problem could be solved by preparation a mixed support which combines suitable properties of SiO_2 and TiO_2 together in one material. The first attempts of preparation titano-silicates [16, 18, 49, 50] were not prepared in titanium content higher than 9 wt.% [50] which is still too low for obtaining sufficient activity in ODH reaction requiring for industrial using (VII).

We report one-pot synthesis of Ti-HMS support with high content of titanium (6 and 19, respectively) (VII). In this case we obtained hexagonal mesoporous silica support with the isomorphously exchanged titanium oxide species and this is evidenced from DR UV-vis spectra in Figure 11. These species serve like an “anchor” for vanadium active species. The main reason for this behaviour is probably the difference in the isoelectric point of TiO_2 (IEP = 6–6.4) and SiO_2 (IEP = 1–2) supports. The acidic vanadium oxide species (IEP = 1.4) are preferentially bonded to the surface hydroxyls of more basic TiO_2 [10].

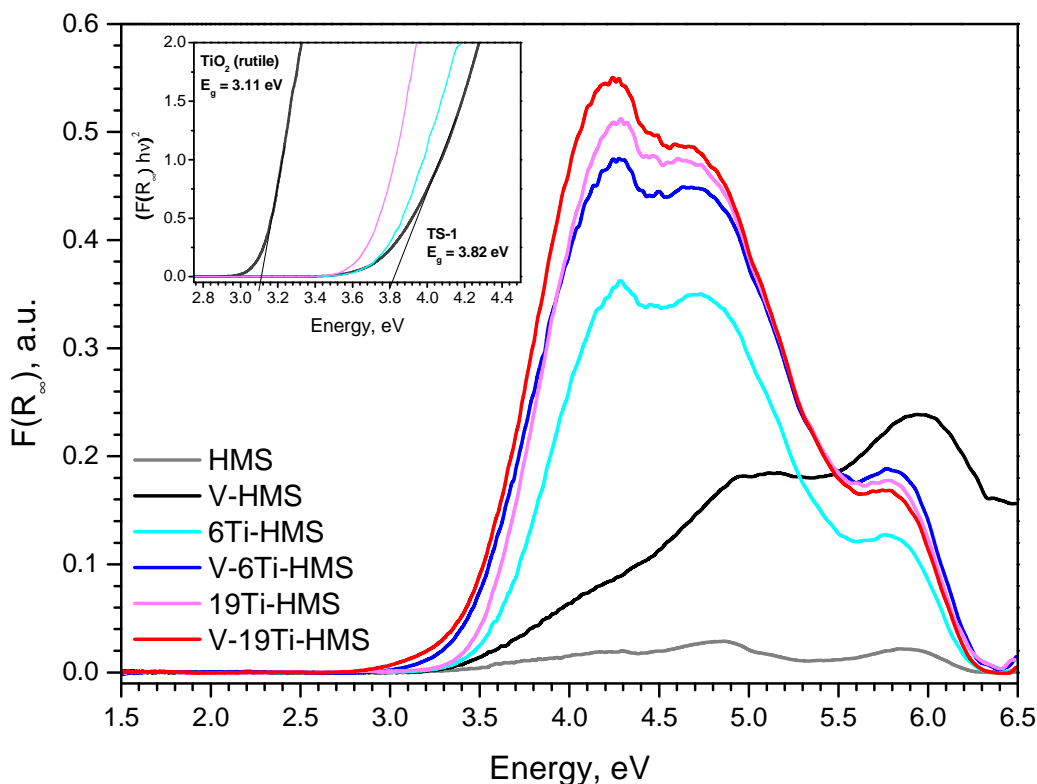


Figure 11 – DR UV-vis spectra of dehydrated supports and final catalysts with vanadium content about 1.5 wt.%. The x in xTi-HMS is the titanium content in wt.% (VII).

Moreover, acid/base properties of titanium species in the support influence the strength of the bridging oxygen in Ti-O-V and therefore their reactivity. The high reactivity of V-Ti-HMS catalysts allows carry out the reaction at significantly lower temperature (460 °C) then in the case of V-HMS catalysts. The Figure 12 shows that the selectivity to $\text{C}_{4\text{-deh.}}$ products is comparable for both catalytic systems (V-HMS and V-Ti-HMS, respectively) and it is about 50 %. However, the activity of V-Ti-HMS catalysts is significantly higher in comparison with V-HMS, even at lower reaction temperature (IV). However, the productivity of V-Ti-HMS catalyst is still to low in

comparison with our most performing catalysts V-SBA-15 prepared by direct synthesis (VI, VII).

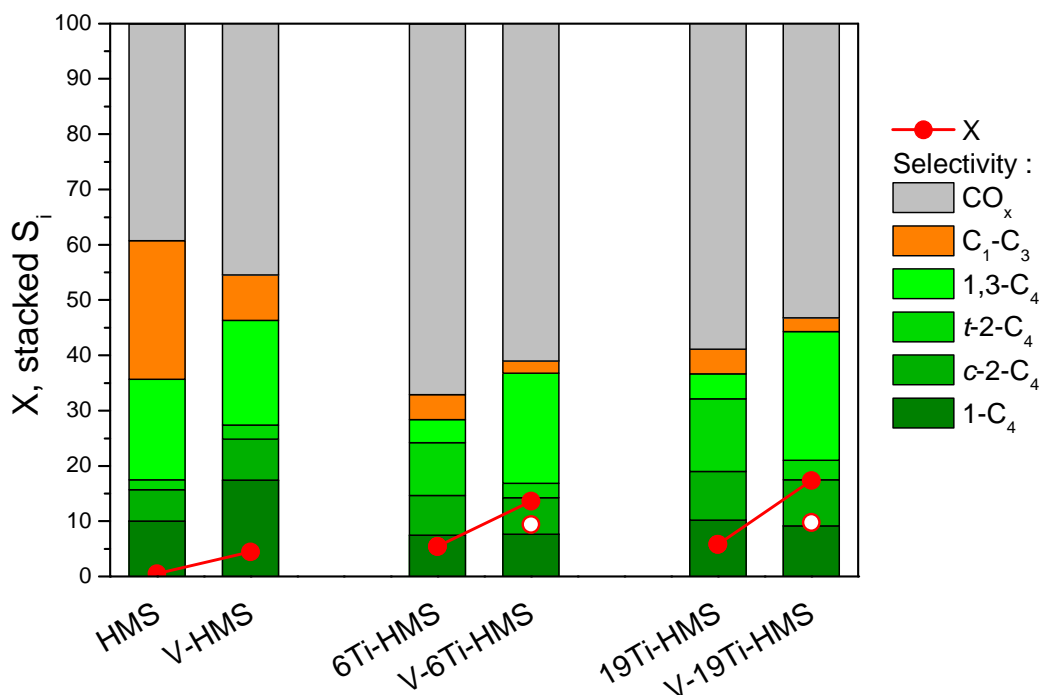


Figure 12 – The conversion (full red circle and line), hypothetical conversion (hollow red circle point) and selectivity (stacked bar) of bare supports and support with impregnated VO_x (1.5 wt.%) in ODH of *n*-butane at 460 °C (VII).

5 Conclusions

This doctoral thesis contributed to the general knowledge about vanadium oxide supported on silica and their using in ODH of *n*-butane and the main results can be summarized as follows:

- It is necessary use combination of more characterization techniques for proper catalyst characterization.
- DR UV–vis spectroscopy provides the most detailed information about VO_x speciation on silica based supports but for the correct results it is necessary to dilute the vanadium containing samples by pure silica (ratio 1:100). Intensity of obtained spectra of the diluted samples is proportional to overall concentration of vanadium what allows us to use deconvolution of spectra to individual spectral bands and offers the possibility to obtain more detailed and semi–quantitative information about speciation of supported VO_x species.

- The Raman spectroscopy is very sensitive technique for monitoring of V_2O_5 microcrystallines but the using of several excitation wavelengths is recommended for more accurate characterization of dispersed vanadium complexes. No information about T_d coordinated VO_x particles speciation was founded in Raman spectra due to strong vanadium silicon vibration coupling.
- The monomeric units with T_d coordination are the most active and selective catalytic sites in *n*-butane ODH in comparison with all other species which we can found on the surface. Moreover C_4 -ODH reaction is very sensitive to presence of isolated vanadium species and can be used as a “probe reaction” for their investigation.
- The VO_x species with higher degree of polymerization participate mainly in undesired consecutive reactions with of ODH products.
- The method of preparation influences the formation of oligomeric species. The impregnated samples contain higher amount of O_h coordinated species compared to samples prepared by direct synthesis.
- SBA-15 support is the most suitable structure for deposition of vanadium in the form of isolated T_d coordinated monomeric species.
- The V-SBA-15 material prepared by direct synthesis belongs to three catalysts with highest C_{4-deh} productivity values which were published for ODH of *n*-butane in literature.
- Introduction of titanium to the silica walls led to catalysts with proper selectivity and high activity even at lower temperature (460 °C) in comparison with pure silica based materials without significantly negative effects to C_{4-deh} selectivity observed on the pure TiO_2 based supports.

6 Published results

- I) M. Setnička, P. Čičmanec, R. Bulánek
DR UV-Vis and H₂-TPR characterization of the supported vanadium oxide catalysts
10th Pannonian international symposium on catalysis, Kraków, Poland, 45-51, 2010,
ISBN 978-83-929430-4-4
- II) R. Bulánek, L. Čapek, M. Setnička, P. Čičmanec
DR UV-vis Study of the Supported Vanadium Oxide Catalysts
The Journal of Physical Chemistry C, **115**, 12430-12438, 2011
- III) R. Bulánek, P. Čičmanec, M. Setnička
Possibility of VO_x/SiO₂ complexes speciation: comparative multi-wavelength Raman and DR UV-vis study
Physics Procedia, DOI: 10.1016/j.phpro.2013.04.024, 2013
- IV) M. Setnička, R. Bulánek, L. Čapek, P. Čičmanec
n-Butane oxidative dehydrogenation over VO_x HMS catalyst
Journal of Molecular Catalysis A: Chemical, **344**, 1-10, 2011
- V) R. Bulánek, A. Kalužová, M. Setnička, A. Zukal, P. Čičmanec, J. Mayerová
Study of vanadium based mesoporous silicas for oxidative dehydrogenation of propane and n-butane
Catalysis Today, **179**, 149-158, 2012
- VI) M. Setnička, P. Čičmanec, R. Bulánek, A. Zukal, J. Pastva
V-SBA-15 prepared by direct synthesis as high performing catalyst in oxidative dehydrogenation of n-butane
Catalysis Communications, under revision
- VII) M. Setnička, P. Čičmanec, R. Bulánek, A. Zukal, J. Pastva
Hexagonal mesoporous titanosilicates as support for vanadium oxide – Promising catalysts for the oxidative dehydrogenation of n-butane
Catalysis Today, **204**, 132-139, 2013

Results of our research were presented by 3 oral and 23 poster presentations on 19 international scientific meetings.

7 References

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