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**UV-VIS DIFFUSE REFLECTANCE SPECTRA
OF VANADIUM-BASED CATALYSTS:
POTENTIALITIES OF THE PRAYING MANTIS
DIFFUSE REFLECTANCE ACCESSORY**

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The aim of work is to study the vanadium-oxo species at V-alumina and V-silica catalysts by using of praying Mantis diffuse reflectance accessory, which enables to measure the spectra under reaction conditions. Firstly, we had focused on the elimination of setting problems with the praying Mantis diffuse reflectance accessory. Secondly, we analysed the distribution of vanadium-oxo species at V-silica and V-alumina catalysts under oxygen atmosphere and under C2-ODH reaction conditions. It has been observed that the degree of vanadium polymerisation was higher on V-alumina in comparison to V-silica. The degree of polymerisation decreased at V-alumina and V-silica materials under presence of C2-ODH reaction conditions in comparison to the oxygen atmosphere.

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Introduction

Supported vanadium-based catalysts are attractive catalysts applicable in many oxidation reactions, such as ammoxidation of alkyl aromatics, selective catalytic reduction of NO_x with NH_3 , oxidation of SO_2 to SO_3 , oxidative dehydrogenation of alkanes to olefins, and selective oxidation of methanol to formaldehyde [1].

In spite of intensive research, the analysis of the distribution of vanadium-oxo species at the supported vanadium-based catalysts is still matter of interest. In general, there are three different types of vanadium species present on the surface of supports; namely: (i) isolated monomeric tetrahedral VO_4 species linked by three V-O bonds with the support at the dehydrated state, (ii) the oligomeric/polymeric VO_x species with distorted tetrahedral symmetry bonded by bridging V-O-V bonds, and (iii) 2D/3D crystalline V_2O_5 nanoparticles [2-5]. The distribution of vanadium-oxo species has been analysed by using of diffuse reflectance spectroscopy [2,6-8], Raman spectroscopy [9], temperature program desorption of hydrogen (H_2 -TPR) [6,10], IR-spectrometry [8], XRD [8,10], ESR [6], solid state ^{51}V NMR [6,11], and XPS [8].

However, it is commonly accepted that the species present at as-prepared catalysts could be redistributed under reaction condition to another type of the active sites. Thus, high effort is recently focused on the characterisation of such active sites under reaction conditions [12]. *In-situ* Raman [10,13], IR [14] and diffuse reflectance [15,16] spectroscopies represent the powerful tools to analyse the presence of vanadium-oxo species under reaction conditions.

Diffuse reflectance UV-Vis spectroscopy provides information on the nature and oxidation state of vanadium oxo-species. This technique is relatively widespread and sensitive to the occurrence of individual types of vanadium-oxo species. Positions of the individual bands are dependent on the vanadium oxidation state and coordination. V(V) species are characteristic by the presence of bands in a region of 200-800 nm (6.20-1.55 eV) [17]. Moreover, this technique enables quantitative analysis of the amount of individual VO_x species. On the other hand, the disadvantage of this technique is the rise of relatively broad bands in the spectra, which may sometimes complicate the detailed interpretation of the spectra. In this work, we have focused on the analysis of the vanadium-oxo species present at V-alumina and V-silica catalysts by using of praying Mantis diffuse reflectance accessory, enabling to measure the spectra under reaction conditions. Firstly, we paid attention to the elimination of some setting problems of praying Mantis diffuse reflectance accessory. In order to fulfil this aim, several partial problems had to be solved. We compared and discussed the differences in the spectra measured with the BaSO_4 -coated integrating sphere and praying Mantis diffuse reflectance accessory. The *in-situ* spectra and catalytic activity are usually measured at two different devices. In order to measure both spectra and catalytic activity in one moment, we utilised a technical possibility to connect the praying

Mantis diffuse reflectance accessory with the GC analysis. Then, we focused on the analysis of vanadium-oxo species present in V-alumina and V-silica catalysts under oxygen presence and under C2-ODH reaction conditions.

Experimental

Preparation of Catalysts

Alumina support (3×6 mesh, 6.7×3.3 mm) was supplied by Eurosupport. Hexagonal mesoporous silica (HMS) was synthesised according to the procedure reported by Tanev and Pinnavaia [18]. HMS (835 m² g⁻¹, average pore diameter 3.7 nm) was prepared by dissolving of 13.6 g dodecylamine (DDA, Aldrich) in the mixture of 144.6 ml ethanol and 200 ml re-H₂O (re-distilled water). After stirring for 20 min, 56 ml tetraethylorthosilicate (TEOS, Aldrich) in 81 ml ethanol was added drop-wise and stirred. The reaction was performed at room temperature for 18 hours under static conditions. The solid product was filtered, washed with water and finally treated in air at 450 °C for 8 hours.

V-alumina and V-silica catalysts were prepared by impregnating HMS and alumina support with the solution of vanadyl(IV) acetylacetonate in ethanol. After impregnation, the catalysts were filtered and dried for 24 hours at room temperature. Calcination was carried out for 8 hours at 600 °C in the air atmosphere.

Characterisation of Catalysts

The vanadium content was determined by means of ED XRF by ElvaX (Elvatech, Ukraine) equipped with a Pd anode. Samples were measured against the model samples (a mechanical mixture of pure SiO₂ and NaVO₃) granulated to the same size as catalysts. Surface area was determined from the nitrogen adsorption/desorption isotherms measured at 77 K using the ASAP 2020 instrument (Micromeritics, USA). The surface vanadium density (VO_x surface density, VO_x nm⁻²) was calculated as $\frac{N_A w_V}{M_V S_{BET}} \times 10^{-18}$, where N_A is Avogadro constant, w_V is the mass fraction of vanadium in V-catalyst, M_V is molecular weight of vanadium (50.94 g mol⁻¹) and S_{BET} is the specific surface area of V-modified catalyst (m² g⁻¹).

Firstly, the UV-vis diffuse reflectance spectra were recorded using GBS CINTRA 303 spectrometer (GBC Scientific Equipment Pty Ltd., Australia) equipped with BaSO₄-coated integrating sphere. Spectralon[®] disc was used as

reference material. The spectra were recorded in the range of 200-850 nm (with lamps switched at 350 nm). The setting parameters were: slit width 2 nm, scan speed of 60 nm min⁻¹, and step size of 1 nm. Spectra of pure or diluted as-prepared V-materials were measured. The samples were diluted by pure silica (fumed silica, Aldrich) at a ratio of 1:100 to avoid the spectra detection limits overflow and to give better resolution of individual spectral bands [7].

Secondly, the UV-vis spectra were recorded using Evolution 300 UV-Vis Spectrophotometer (Thermo Scientific) equipped with the praying Mantis diffuse reflectance accessory. Praying Mantis diffuse accessory used two 6:1 90° off-axis ellipsoidal mirrors. Such an optical geometry permits to collect up to 20 % of all diffused reflected radiation. These spectra were recorded in the range of 200-850 nm (lamps at 350 nm). The setting parameters were: slit width 4 nm, scan speed of 60 nm min⁻¹ and step size of 1 nm. Firstly, we measure the spectra of pure or diluted as-prepared V-materials. Secondly, we measure the spectra of V-materials under oxygen atmosphere. Feed composition was 2.5 vol. % oxygen in helium). Finally, we measure the spectra of V-materials under C2-ODH reaction conditions. Feed composition was 7.5 % C₂H₆, 2.5 % O₂ and 90 % He; the total flow rate being 25 ml min⁻¹. Main limit of praying Mantis diffuse reflectance accessory is a temperature at 600 °C in vacuum (when the maximal temperature decreases in the presence of oxygen).



Fig. 1 Praying Mantis diffuse reflectance accessory. Experimental set-up

Figure 1 shows the praying Mantis diffuse reflectance accessory. There were several technical problems that had to be solved before measurements. Firstly, the cooling of reaction cell had to be sufficient. The cooling of the praying Mantis diffuse reflectance accessory was accomplished by central cooling system being capable of keeping the temperature of water at the output from the reaction cell below 30 °C. Second problem then represented a possible leakage of reaction cell, which could lead to the presence of air in the reaction gas and in varied concentration of oxygen with inaccurate GC analysis. Therefore, we carefully checked the possible leakage of reaction cell before the starting of experiments; in our case of the praying Mantis diffuse reflectance accessory using the GC configuration. In the absence of leaking, the nitrogen was not present at the reaction mixture at low total flow rate. The spectra under reaction conditions were usually collected under such experimental conditions as close as for those used during the catalytic tests, and suggesting that the catalyst exhibits the same propelling behaviour at both experimental arrangements. However, the most difficult problem was to keep the same contact time in both systems. Therefore, we have connected the praying Mantis diffuse reflectance accessory with GC to be able of measuring the actual activity of the catalysts tested at the same time whilst the spectra were recorded. This connection required the control of pressure impacts and the respective change in catalyst position in the cell.

At both experimental setups, the samples were granulated and sieved to a fraction of 0.25-0.5 mm in mesh. Finally, the reflectance was re-calculated to the absorption by using the Schuster–Kubelka–Munk equation, $F(R_\infty) = \frac{(1 - T_\infty)^2}{2R_\infty}$ where R_∞ is the diffuse reflectance from a semi-infinite layer.

Results and Discussions

Elimination of the Setting Problems of Praying Mantis Diffuse Reflectance Accessory

Figure 2 shows comparison of the normalized UV-vis spectra of as-prepared V-HMS with 9 wt.% V measured with a BaSO₄-coated integrating sphere and praying Mantis diffuse reflectance accessory. There were two main differences at both spectra, the opposite intensity of bands at 3.3 eV and 4.9 eV, and the absence of band at 5.8 eV in the spectra measured with praying Mantis diffuse reflectance accessory.

Firstly, the band at 3.3 eV was observed at both spectra. Although the band with maxima at 4.9 eV was also noticed at both spectra, this band could be clearly identified only at the spectra measured by the praying Mantis diffuse reflectance

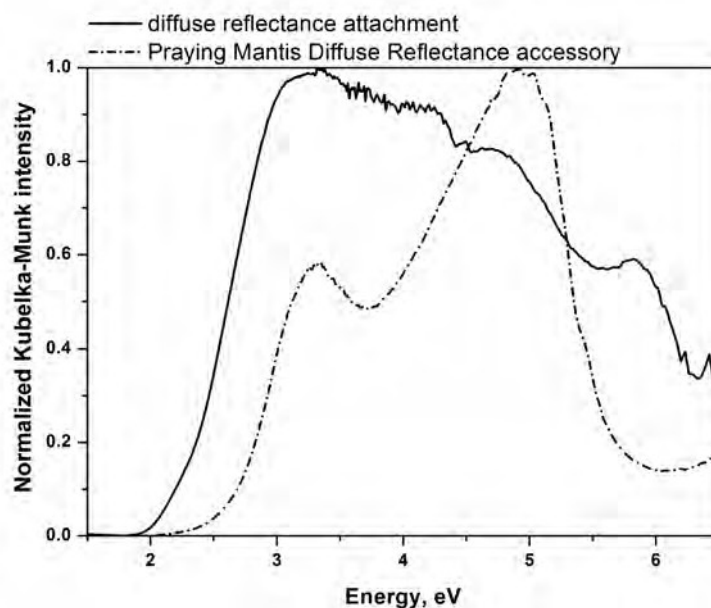


Fig. 2 Normalized UV-vis spectra of as-prepared V-HMS with 9 wt. % V measured with diffuse reflectance attachment and praying Mantis diffuse reflectance accessory

accessory. In the case of BaSO₄-coated integrating sphere, the band was present as a shoulder of the dominant band at 3.3 eV. This discrepancy can be explained by nonlinear dependence of Kubelka–Munk intensity on the concentration of the individual types of vanadium species. More specifically, as previously reported by Bulánek *et al.* [7], the intensity of each band is characterised by another region of linear dependence between Kubelka–Munk intensity and the concentration of contributing vanadium species (the linear dependence is valid for different region. After that, Kubelka Munk intensity limits to a different value). Moreover, the praying Mantis diffuse reflectance accessory operates only with a small fraction of spectra intensity in comparison with that of BaSO₄-coated integrating sphere. Thus, it can be supposed that both instruments exhibit different divergences from the linear dependence between Kubelka–Munk intensity and the concentration of VO_x species. At this moment, we did not pay attention to the quantitative analysis of the individual VO_x species in the praying Mantis diffuse reflectance accessory measuring mode. However, Fig. 3 compares the spectra of pure and diluted as-prepared V-HMS catalyst with 9 wt. % V. It is clearly seen that the spectra of diluted materials are more close each to other. Slight differences in both spectra can be attributed to the collection of different amount of diffused reflected radiation. While BaSO₄-coated integrating sphere permits one to apply all diffused reflected radiation, the praying Mantis diffuse reflectance accessory is able of collecting up to 20 % of all diffused reflected radiation.

The fact that there was the opposite intensity of bands at 3.9 and 4.9 eV in the spectra of pure (Fig. 2) and diluted (Fig. 3) materials supports the previously

mentioned suggestion that the dependence of the band intensity on the concentration of corresponding vanadium site is linear only at the limited vanadium content. Moreover, every band is characteristic by the different region of linear dependence. Thus, it can be concluded that the measurement of the spectra of non-diluted V-based catalysts primary results in the qualitative information about the presence of the individual types of VO_x species. And deconvolution and quantitative analysis of the amount of VO_x species is then possible only in the spectra of diluted sample of V-material.

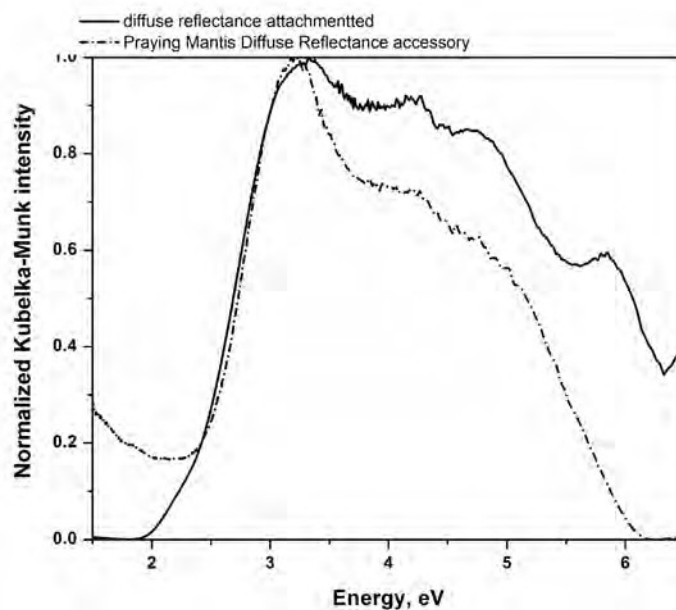


Fig. 3 Normalized UV-vis spectra of as-prepared diluted V-HMS with 9 wt. % V measured with diffuse reflectance attachment and praying Mantis diffuse reflectance accessory

Secondly, Fig. 2 shows the difference in the absorption between 5.5 and 6.0 eV for both experimental arrangements. While the spectra measured with BaSO_4 -coated integrating sphere had exhibited the presence of low intensive band at 5.8 eV, no absorption was noticed in the spectra obtained in the praying Mantis diffuse reflectance accessory mode. This observation could be associated with the different way of spectra collection.

As indicated by the term itself, BaSO_4 -coated integrating sphere uses barium sulphate, where the signal could be affected by the co-absorption of BaSO_4 above eV. On the other hand, the praying Mantis diffuse reflectance accessory uses the optical geometry with the ellipsoidal mirrors, where the BaSO_4 surface does not contribute. Figure 4 shows the same profile of spectra for V-HMS with 9 wt. % V measured against BaSO_4 and Spectralon reference materials, which indicates no contribution of the latter. In this case, it can be concluded that the UV-vis diffuse reflectance spectra measured by using of BaSO_4 -coated integrating sphere could be affected by the co-absorption of BaSO_4 in the range of 5.5-6.0 eV. The-

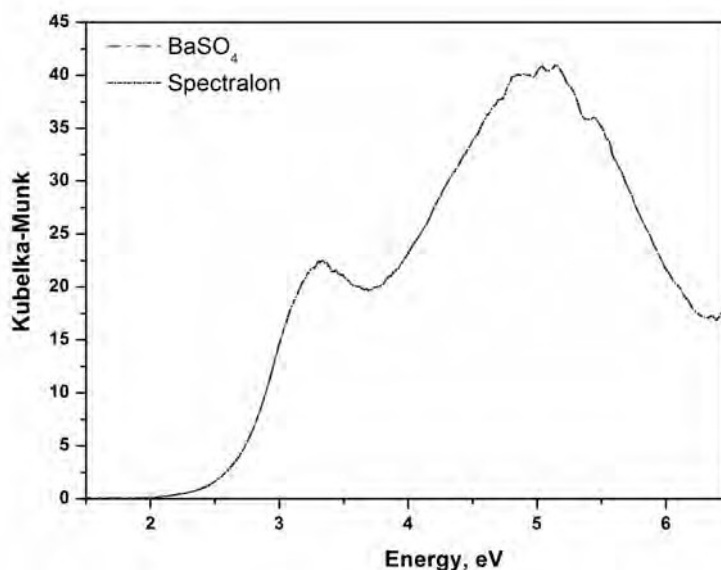


Fig. 4 UV-vis spectra of as-prepared V-HMS with 9 wt. % V measured praying Mantis diffuse reflectance accessory against BaSO₄ and Spectralon as reference material

refore, it is necessary to be careful in the interpretation of the spectra in that region as the band observed in this region could originate from the sample, but — at the same time — $\frac{3}{4}$ from the background of BaSO₄-coated integrating sphere. Thus, this region of the spectra cannot be used to simply extrapolate the results between both types of instruments.

Figure 5 shows the *in-situ* spectra of V-HMS material with 9 wt. % V at vacuum measured from 25 °C to 450 °C, when the image A depicts the results obtained with the original set up. As clearly seen, the spectra of V-HMS catalyst are affected by another phenomenon, not originating from the absorbance of VO_x species. We have found out that this problem is caused by the thermal expandability of net during the heating of sample in the praying Mantis diffuse reflectance accessory. While at room temperature, the baseline and the spectra of sample were collected from the straight surface, a small change in the sample position in the cell was observed during the heating of sample; see the inset in Fig. 5A. In other words, the spectra measured at higher temperature were affected by changing position of sample. Firstly, it resulted in the reflection of the spectra due to non-ideal surface of the sample and, secondly, the spectrum of sample was shot at the different position with the respect to the reference material, which originated in the different amount of collected signal of all diffused reflected radiation. Thus, we mechanically set down the original diameter of the net (3 mm). Figure 5B then shows the spectra of V-HMS catalyst with 9 wt. % of V collected on praying Mantis diffuse reflectance accessory after decrease in the net diameter. In this case, the intensity of the band at 3.3 eV decreased whereas the intensity of the absorption between 4-6 eV increased with higher temperature. Hence, this chan-

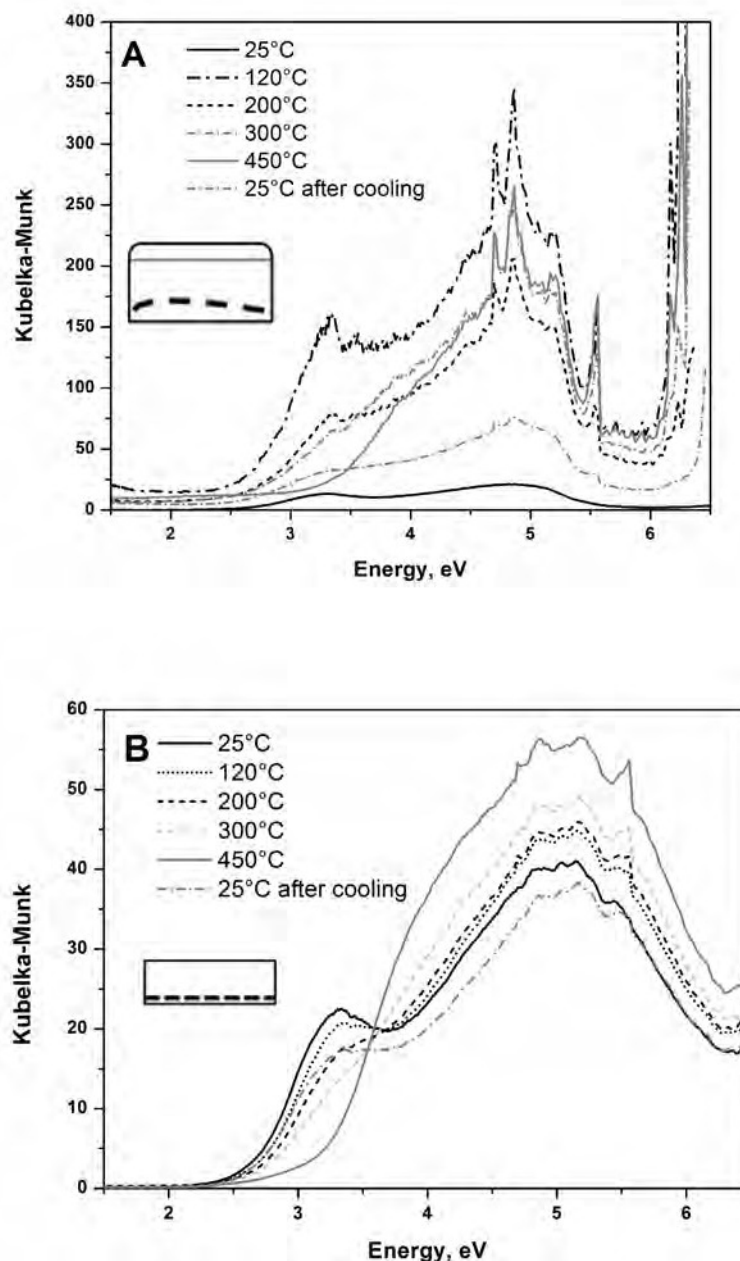


Fig. 5 In-situ spectra of V-HMS material with 9 wt. % V at vacuum and temperature 25-450 °C. (A) measured with the original set-up and (B) measured after decreasing the net diameter

ge in the intensity of both bands could be attributed to the dehydration of V-HMS catalyst. When the temperature was coming back to the room temperature, the intensity of both bands returned to its original profile, but the whole process had not been fully completed during 600 min; i.e., at the time for which the spectrum was collected after cooling the system down to room temperature. Again, the change in intensity of bands at 3.3 eV and 4-6 eV was due to the dehydration and re-hydration of V-HMS material.

VO_x Species Present on V-alumina and V-silica Catalysts

Figure 6 illustrates the spectra of V-HMS and V-alumina catalysts at 500 °C in the oxygen atmosphere and measured again with the aid of the praying Mantis diffuse reflectance accessory. The temperature of 500 °C represents the compromise between the sufficient activity of V-based catalysts and the thermal resistance of the technique used. It is clearly seen that the spectrum of both materials is significantly affected by the background / noise in the range of 4.5-6.0 eV. In literature, high effort is paid to the assignment of UV-vis bands to the individual VO_x species. Several authors attempted to explain one or two absorption bands by the existence of *T_d* (or *C_{3v}*) oligomeric units in the range 3.37-4.22 eV [17,19] and one, two, or three absorption bands due to the occurrence of *T_d* monomeric units in the range of 3.50-5.77 eV [20,21]. Previously [7], we attributed the band at 5.9 eV to the presence of isolated monomeric VO_x units, the band at 4.6-5.1 eV to the isolated monomeric and oligomeric tetrahedrally coordinated VO_x species, and the band at 3.75-4.1 eV to the *T_d* coordinated oligomers. From that point of view, the spectra shown in Fig. 6 could be useful only in the region of 1.5-4.5 eV. In spite of this restriction, the difference in the spectra of V-HMS and V-alumina catalysts with the same V loading (9 wt. % V) is evident. The spectrum of V-alumina exhibited significantly lower value of absorption edge energy in comparison with the spectrum of V-HMS catalyst. The evaluation of the edge of the absorption energy apparently resulted in the analysis of the presence of particular VO_x species [2,20,22,23]. The absorption edge energies lie within the defined range for the model pseudotetrahedral compound and V₂O₅ (2.48 eV) [24]. Thus, V-alumina catalyst contained a relatively higher abundance of octahedrally coordinated VO_x species in comparison with the V-HMS material. This could be due to the different theoretical monolayer capacity and different polymerization of VO_x species on silica and alumina supports.

The VO_x surface density was 4.2 VO_x nm⁻² for V-HMS and 7.1 VO_x nm⁻² for V-alumina. The theoretical monolayer capacity for isolated monomeric VO_x species was reported to be ~0.7 VO_x for nm⁻² SiO₂ [1] and 7-8 VO_x nm⁻² for Al₂O₃ [1]. At silica, isolated monomeric VO_x species represent the main type of VO_x species formed below monolayer capacity [25]. From that point of view, the formation of polyvanadate species could be expected on V-HMS with 9 wt. % V, as this material exhibited higher VO_x surface density (4.2 VO_x nm⁻²) compared to the theoretical monolayer capacity for isolated monomeric VO_x (~0.7 VO_x nm⁻² for SiO₂ [1]). It should be mentioned that the value of VO_x surface density (4.2 VO_x nm⁻²) observed for V-HMS with 9 wt. % V is lower than that previously reported by us to similar V-HMS material [26]. This could be caused by preparation of a new V-HMS sample originating from another HMS support and because of the fact that the VO_x surface density had dramatically increased with vanadium loading above 4 wt. % V [26], when the value of VO_x surface density could be sensitive to the process of synthesis of V-materials with such a high vanadium

loading. On the other hand, V-alumina with 9 wt. % V exhibited the VO_x surface density $7.1\text{VO}_x \text{ nm}^{-2}$, which is a value close to the theoretical monolayer capacity for isolated monomeric VO_x ($7\text{--}8 \text{ VO}_x \text{ nm}^{-2}$ for Al_2O_3 [1]). However, VO_x polymerisation could also be expected at V-alumina with 9 wt. % V, because it might proceed at alumina support below the the monolayer surface coverage.

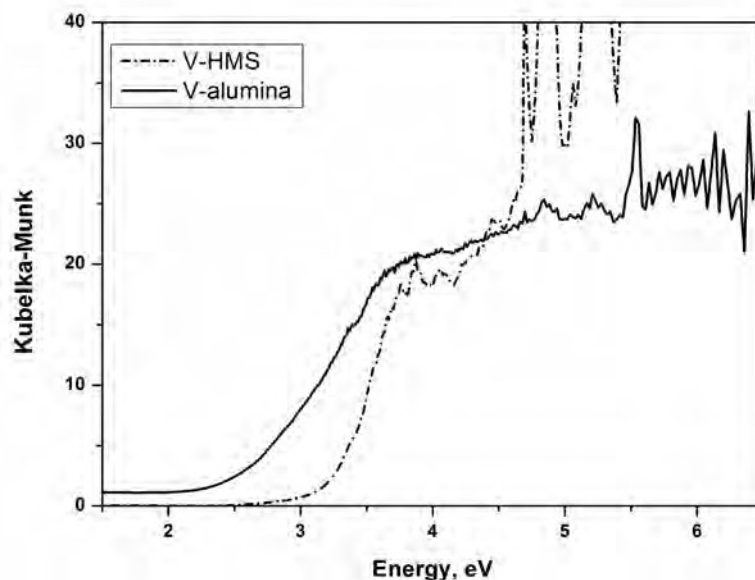


Fig. 6 In-situ spectra of V-HMS and V-alumina materials with 9 wt. % V catalysts at 500 °C under oxygen atmosphere (2.5 vol. % O_2 in He) measured by using of praying Mantis diffuse reflectance accessory

Analysis of VO_x Species Redistribution under C2-ODH Reaction Conditions

Figures 7 and 8 show the spectra of V-HMS with 9 wt. % V (Fig. 7) and V-alumina with 9 wt. % V (Fig. 8) in the atmosphere of oxygen in helium and under C2-ODH reaction mixture. The temperature was 500 °C in both experiments. Table I surveys the corresponding productivity of ethene for V-HMS and V-alumina catalysts in the oxidative dehydrogenation of ethane. As expected, the ethylene productivity was higher for V-alumina than that for V-HMS [2,27-29]. Thus, the most important result is that the addition of ethane has resulted in the increase in absorption edge energy for both V-alumina and V-HMS materials. It also shows that the polymerisation degree of vanadium had decreased after the addition of ethane, i.e., under C2-ODH reaction conditions and if being compared to the V-HMS and V-alumina catalysts under oxygen atmosphere. In spite of relatively low catalytic activity of the V-HMS at 500 °C, the significant change in the profile of spectra for the material studied reveals rather high potential of the praying Mantis diffuse reflectance accessory in the study of active vanadium species at C2-ODH reaction.

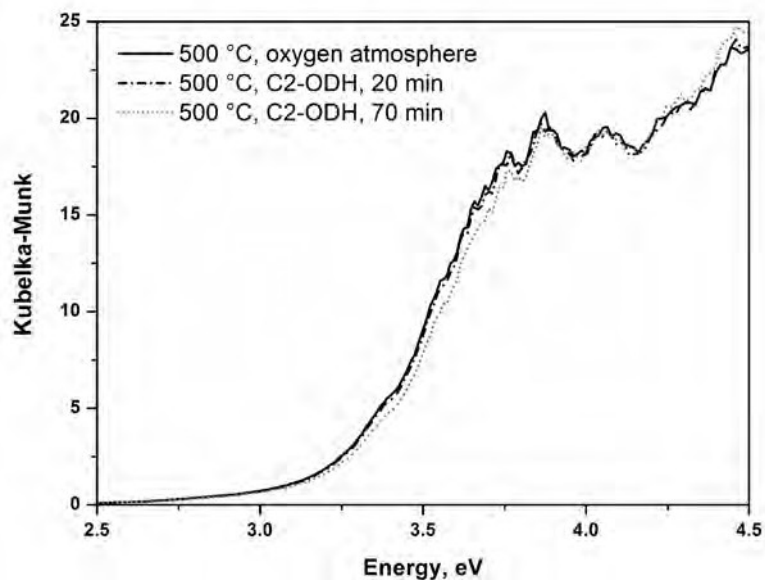


Fig. 7 In-situ spectra of V-HMS catalyst with 9 wt. % V catalysts at 500 °C under oxygen atmosphere (2.5 vol. % O₂ in He) and at oxidative dehydrogenation of ethane (C2-ODH, 2.5 % O₂, 7.5 % C₂H₆ in He) measured by using of praying Mantis diffuse reflectance accessory

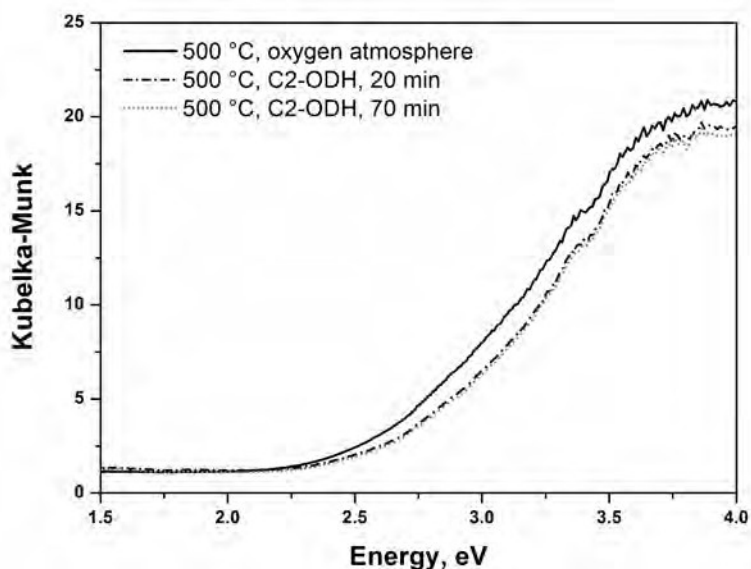


Fig. 8 In-situ spectra of V-alumina catalyst with 9 wt. % V catalysts at 500 °C under oxygen atmosphere (2.5 vol. % O₂ in He) and at oxidative dehydrogenation of ethane (C2-ODH, 2.5 % O₂, 7.5 % C₂H₆ in He) measured by using of praying Mantis diffuse reflectance accessory

Table I Chemical and textural properties of V-HMS and V-alumina catalysts. Ethene productivity achieved for V-HMS and V-alumina catalysts in the ODH of ethane

	wt. % V	S_{BET} $m^2 g^{-1}$	VO_x surface density $VO_x nm^{-2}$	Productivity of ethene $g(C_2H_4) g_{cat}^{-1} h^{-1}$
V-HMS	9	255	4.2	0.06
V-alumina	9	150	7.1	0.22

Conclusion

A critical comparison of the praying Mantis diffuse reflectance accessory with the $BaSO_4$ -coated integrating sphere has resulted in the following conclusions:

- The measurement of the spectra of non-diluted V-based catalysts primarily offers qualitative information about the presence of the individual types of VO_x species. Deconvolution and quantitative analysis of the amount of VO_x species is possible only in the spectra of diluted sample of V-material.
- The UV-vis diffuse reflectance spectra measured by using of $BaSO_4$ -coated integrating sphere could be affected by co-absorption of $BaSO_4$ in the range of 5.5-6.0 eV. Thus, one has to be careful to interpret the spectra in that region when the band observed in this region could originate from the sample, but — at the same time — it can also be due to the effect of the background of $BaSO_4$ -coated integrating sphere.

Furthermore, as found out, V-alumina has offered a higher degree of polymerisation of VO_x species in comparison with the V-HMS material. This effect has been attributed to the different monolayer capacity of alumina and silica materials, as well as to the different polymerisation of VO_x species on silica and alumina supports. Finally, the addition of ethane has given rise to an increase in absorption edge energy and its value(s) for both V-alumina and V-HMS material.

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