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Possibility of VO_x/SiO₂ complexes speciation: comparative multi-wavelength Raman and DR UV-vis study

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Abstract

Raman spectroscopy is one of the very often used spectroscopic methods for characterization of vanadium surface species. However, Raman spectra of VO_x-silica systems are more complex and interpretation is more difficult in comparison with other supports (like Al₂O₃, ZrO₂, TiO₂ or Nb₂O₅) because there is strong vibrational coupling between the vanadia species and the silica support. Therefore, assignment and interpretation of some vibrational bands is still subject of controversy. This fact results in incongruity of suggested molecular structure and population of individual vanadium surface complexes. In this contribution, we present systematic comparative study of diffuse reflectance UV-vis spectra and Raman spectra excited by 325 and 514.5 nm lasers obtained on set of dehydrated vanadium modified hexagonal mesoporous silica (VO_x-HMS) samples with vanadium loading from 2 up to 12 wt. %. We prove that changes in population of oligomeric and monomeric VO_x species in individual samples are not manifested by significant changes in the character of Raman signals. On the other hand it is evident that with increasing of vanadium loadings the UV-vis spectra show systematic changes. Raman spectroscopy is useful characterization technique for detection presence of very small amount of V₂O₅ microcrystallites, especially if suitable wavelength of laser is used for remarkable resonant enhancement of Raman intensity of its bands (e.g. 514.5 nm).

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Keywords: vanadium; catalyst; diffuse-reflectance UV-vis spectroscopy; Raman spectroscopy; speciation;

1. Introduction

Supported vanadium oxide plays important role as catalysts for the selective oxidation of hydrocarbons or alcohols [1, 2]. Knowledge of the prevailing molecular structure of surface vanadium species is essential for understanding the structure – catalytic activity relationship. Supported catalysts are complex

materials and the determination of active surface species and their structure is challenging task. To this end, characterization of VO_x species present on the surface of oxidic supports has been the subject of many spectroscopic studies including Raman, electron paramagnetic resonance (EPR), diffuse reflectance spectroscopy in the visible and ultraviolet region (DR UV-vis), nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), extended X-ray absorption fine structure (EXAFS) spectroscopy [3-19]. Raman spectroscopy is one of the most often used techniques, but structure information is obtained only indirectly and relies on a correct assignment of the observed bands to vibration modes. In the case of silica supported vanadium catalysts, recent experimental and theoretical studies indicated that there is strong vibrational coupling between the vanadia species and the silica support [20-22]. Vibrations of VO_x species cannot be separated from those of the silica support due to coupling between bulk phonons and motions of the supported vanadium complexes which makes Raman spectra of VO_x-silica systems quite complex and interpretation is relatively difficult. Therefore, assignment and interpretation of some vibrational bands is controversial. For example, band at around 920 cm⁻¹ was assigned to V-O-V mode of polymeric species [23, 24], V-O-support mode [20, 22, 25-27], V=O mode [28] or O-O mode [29, 30]. Band at around 1031 cm⁻¹ was assigned to V=O mode and its shift was ascribed to change in polymerization degree of VO_x surface species. Such systematic shifts to higher wavenumbers were observed in Raman spectra of VO_x on Al₂O₃, ZrO₂, TiO₂ or Nb₂O₅ supports, but no shift of this Raman band was observed on VO_x/SiO₂ systems. This fact was often taken as evidence of presence solely monomeric species on the silica. Contrarily, presence of oligo- and polymeric VO_x species with distorted tetrahedral coordination (group of symmetry T_d or C_{3v}) on mesoporous silicas was recently suggested on the basis of IR study of CO and NO adsorption on reduced VO_x-SBA-15 [16], asymmetry of near edge X-ray absorption fine structure spectral (NEXAFS) band of O 1s core excitation of oxygen atoms centered at 531 eV [31] or shifts of charge transfer (CT) bands in UV-vis spectra of dehydrated samples [10, 19, 23, 32-36]. Very recently, we reported systematical and significant shift of energy band gap in DR UV-vis spectra of several sets of hexagonal mesoporous silica modified by vanadium (VO_x-HMS) catalysts investigated in oxidative dehydrogenation (ODH) of n-butane [9, 11] and propane [8, 9]. For evidence of tetrahedral polymeric VO_x species we adopted methodology applied by Gao et al. [37] for supported vanadium oxide species. This methodology is based on the evaluation of edge of absorption energy ε₀ from UV-vis spectra using the expression introduced by Davis and Mott [38] or by Tauc [39] in the form:

$$(F(R_{\infty}) \cdot h\nu)^2 \propto (h\nu - \varepsilon_0) \quad (1)$$

where F(R_∞) is Kubelka-Munk function, h is Planck's constant (6.626068.10⁻³⁴ m² kg s⁻¹), ν frequency (s⁻¹) and ε₀ is energy of absorption edge. The value of exponent of 2, which suggests direct allowed transition, was adopted from Ref. [37]. This methodology correlates this value with the edge of absorption energy of referent compounds (such as sodium ortho- and meta-vanadate representing isolated monomeric vanadyls and polymeric species with V-O-V bond) or theirs mechanical mixtures with known composition respectively [40]. Relative amount of monomeric and polymeric species in the sample can be evaluated from linear dependence of the ε₀ value between values obtained from spectra of model compounds [40].

In this contribution, we present systematic comparative study of DR UV-vis spectra and Raman spectra at 325 and 514 nm wavelength excitations obtained on set of dehydrated VO_x-HMS samples with vanadium loading from 2 up to 12 wt. % providing wide range of VO_x species population and distribution. We prove that changes in population of oligomeric and monomeric VO_x species in individual

samples are not manifested by significant changes in the character of Raman signals. On the other hand, Raman spectroscopy is extremely sensitive to the presence of very small amount of V_2O_5 microcrystallites, especially if suitable wavelength of laser is used for remarkable resonant enhancement of Raman intensity of its spectral bands (e.g. 514 nm).

2. Experimental

2.1. Catalysts preparation

HMS was prepared according to procedure reported by Tanev and Pinnavaia [41]. 13.6 g of dodecylamine (DDA, Aldrich) was dissolved in the mixture of 225 cm³ ethanol and 200 cm³ double-distilled H₂O. After stirring for 20 min, 56 cm³ of tetraethyl orthosilicate (TEOS, Aldrich) was added dropwise and intensively stirred. The reaction was performed at 25 °C for 18 hours under stirring. The solid product was filtered and then repeatedly suspended in 500 cm³ ethanol and stirred at 25 °C for 1 hour in order to remove major part of DDA from obtained solid. Finally, the solid was calcined in flow of air at 540 °C for 8 hours with heating rate 1 °C min⁻¹.

Vanadium oxo-complexes were doped onto silica support by standard wet impregnation procedure by appropriate amount of ethanol/H₂O solution of vanadyl acetylacetonate (Aldrich). Impregnated samples were dried at 120 °C in air overnight and then calcined at 600 °C for 8 hours in the dry air flow. Vanadium content was determined by X-ray fluorescence spectroscopy (bench-top vacuum wavelength dispersive X-ray spectrometer Spectroscan V, Spectron, Russia). Samples were denoted as S-x where x is the vanadium content in the weight percentage.

2.2. DR UV-vis spectroscopy

The UV-vis diffuse reflectance spectra of diluted and subsequently dehydrated samples were measured using 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 samples were diluted by the pure silica (Fumed silica, Aldrich) in the ratio 1:100 in order to obtain better resolution of individual bands and the linear dependence of spectral area on the concentration of vanadium (for more details see ref [10]). All samples were granulated and sieved to fraction of size 0.25-0.5 mm, dehydrated before the spectra measurement and oxidized in the glass apparatus under static oxygen atmosphere (16-18 kPa) 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.[10]. 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 2 :

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

where R_∞ is the measured diffuse reflectance from a semi-infinite layer [42].

2.3. Raman spectroscopy

Raman spectra excited by vis laser of dehydrated catalysts were measured by a dispersive Labram HR spectrometer (Horiba Jobin-Yvon) interfaced to an Olympus BX-41 microscope. Spectra were excited by 514.5 nm line of an Ar⁺/Kr⁺ laser (Innova 70C series, Coherent). The spectra were recorded by collecting of two scans (scan time 1200 s with resolution 2 cm⁻¹) by Peltier-cooled CCD camera detector. The laser power impinging on the dry sample was 1.2 mW and laser spot diameter was approximately 6 μm. Raman spectra excited by UV laser were measured using dispersive Micro-Raman Renishaw RM 1000 spectrometer equipped with CCD detection. Spectra were excited by 325 nm HeCd laser (~ 3 mW at the sample with laser spot size approximately 6 μm) and two scans were collected (time of scan was 100 s with resolution 4 cm⁻¹). The dehydration and oxidation protocol was the same as for DR UV-vis measurement (see above).

3. Results and Discussion

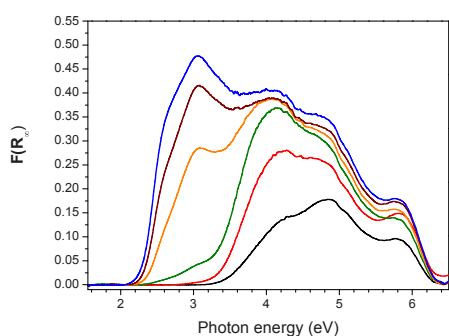


Figure 1 Diffuse reflectance UV-vis spectra of dehydrated VO_x-HMS samples (for assignment of individual curves to the samples see Table 1)

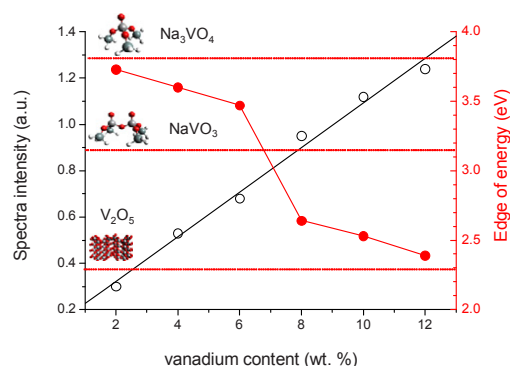


Figure 2 Plot of edge of energy value determined by means of Tauc's law form spectra depicted in the Figure 1 and integral intensity of DR UV-vis spectra vs. vanadium content. Energy edges of model compounds and idealized molecular structure of surface vanadium species are inserted in the plot.

The obtained DR UV-vis spectra for investigated catalyst are presented in the Figure 1. It can be noted that parent HMS support exhibited only very low intensity spectrum without distinct signal and therefore are not reported here. Spectra of VO_x-HMS catalysts contain several absorption bands in region 1.46-6.5 eV (850-190 nm) which are conventionally attributed to ligand to metal charge-transfer (LMCT) transitions of the O → V^{+V} type or to the d-d transitions of V^{+IV} [43]. The d-d absorption bands characteristic for the vanadium(+IV) in the region 1.55 – 2.07 eV [44] were not observed in our spectra and this fact confirms that all vanadium was successfully oxidized to oxidation state (+V) during the pretreatment procedure. The catalysts with concentration higher than 4 wt% of vanadium exhibit absorption bands in the region 2-3 eV with maxima at ca. 2.6 and 3.1 eV and they are attributed to the presence of octahedrally coordinated (group O_h) 2D/3D bulk-like VO_x units [10, 44, 45]. Values of energy of edge (ε₀) determined by Tauc's law (see Eq. 1) are summarized in Table 1 and plotted against vanadium content in the Figure 2. The low-loaded samples exhibit absorption only above 3 eV evidencing

VO_x species with tetrahedral coordination. Samples with vanadium content up to 6 wt.% exhibit edge energy in the range of 3.73 – 3.47 eV (obtained accordingly to Ref. [39]), whereas edge energy of Na₃VO₄, NaVO₃ and V₂O₅ is 3.82, 3.13 and 2.26 eV, respectively. Taking into account this observation, it can be concluded that both isolated VO₄ units and small VO_x aggregates that have V-O-V bonds are present on the surface of these samples (effect of partial hydration was excluded on the base of checking measurement of overtones of OH group vibration on UV-vis-NIR spectrometer, not shown for sake of brevity). Samples with vanadium content higher than 6 wt. % exhibit ϵ_0 below 3 eV and these values systematically decrease with increasing vanadium content and limit to the value of ϵ_0 of bulk oxide. This is in accordance with increasing intensity of absorption bands at 2.6 and 3.1 eV assigned to CT band of V₂O₅ microcrystallites. For quantitative analysis of all three types of surface vanadium complexes, the spectra were deconvoluted into individual bands. Parameters of individual spectral bands used in deconvolution procedure of the spectra was taken from systematic study analyzing wide set of VO_x-HMS samples recently published [10]. The Figure 3 presents examples of the deconvolution of the experimental spectra of sample with and without octahedrally coordinated vanadium complexes. UV-vis spectra of all samples contain three absorption bands in the region 3-6.5 eV and these bands can be attributed to the ligand to metal charge transfers of tetrahedrally coordinated (T_d) species (group of symmetry T_d). The band with maxima position approximately at 4 eV can be attributed to T_d oligomeric species [46, 47]. The band at ca. 5.9 eV belongs to T_d-monomeric species [46-48] and the band with maximum at 5 eV is linear combination of the bands ascribed to both the T_d-monomeric and the T_d oligomeric species. Relative amount of individual VO_x species on the surface was determined from area of corresponding bands (equality of extinction coefficients of individual bands is assumed based on linear dependence of spectra intensity vs. vanadium content in catalysts (see Fig. 2)) and results are given in the Table 1. The low concentrated samples contain only T_d-coordinated VO_x species. The highest relative abundance of isolated monomeric T_d-coordinated units (33 rel. %) can be found on VO_x-HMS with the lowest vanadium content. While relative population of oligomeric T_d-coordinated VO_x species is almost constant (ca. 75 rel. %) , the population of monomeric species decreases with increasing vanadium content from 33 rel. % to 6 rel. % and simultaneously population of octahedrally coordinated species increase from zero to 27 rel. %. This picture is consistent with results of systematic study of Wachs'group which led to conclusion that oxide microcrystallites appeared above monolayer coverage, when all the reactive hydroxyls of the support have been titrated [40, 49]. Monolayer coverage on silica is significantly lower (about 0.7 nm⁻²) in comparison to other supports like alumina, titania and zirconia (about 7–8 nm⁻²). The low surface monolayer coverage on silica is due to somewhat lower density and reactivity of the silica surface hydroxyls in comparison to other oxide supports. Surface vanadium density of our samples range from 0.3 to 24.3 nm⁻², therefore presence of oligomeric T_d- and O_h-coordinated species is reasonable and expectable.

Table 1. List of samples, their physico-chemical characterization, results of DR UV-vis spectra deconvolution.

sample	V content (wt.%)	S _{BET} (m ² /g)	Surface density (nm ⁻²)	ϵ_0 (eV)	Relative population of VO _x complexes			color in Figures
					O _h	T _d ^{oligo}	T _d ^{mono}	
S-2	2.0	760	0.3	3.73	0.00	0.67	0.33	black
S-4	4.0	645	0.7	3.60	0.00	0.70	0.30	red
S-6	6.0	450	1.6	3.47	0.02	0.81	0.17	olive
S-8	8.0	225	4.2	2.64	0.15	0.77	0.08	orange
S-10	10.0	70	17.5	2.53	0.23	0.70	0.08	wine
S-12	12.0	60	24.3	2.39	0.27	0.67	0.06	blue

Figure 4 shows the Raman spectra of a dehydrated S-6 catalyst excited at 514.5 and 325 nm. Evidently, Raman spectrum excited by vis laser is totally different from Raman spectrum excited by UV laser. This is due to the fact that both excitation wavelengths are absorbed by different vanadium species in the sample and therefore different resonance enhancement effect control Raman band intensities. The Raman spectrum excited by 514.5 nm laser exhibits set of bands at 282, 301, 404, 520, 697, and 993 cm^{-1} – a typical fingerprint of V_2O_5 crystallites [50]. Besides these bands, band at 1040 cm^{-1} with small shoulder at 1060 cm^{-1} can be seen. This band is usually assigned to terminal $\text{V}=\text{O}$ stretching vibration, but this assignment has been questioned recently [28]. The shoulder at 1060 cm^{-1} was previously ascribed to silica skeletal vibration ($\text{Si}-\text{O}$ bond vibration) or $\text{Si}(\text{O}^-)_x$ functionalities [51], but recent theoretical work suggests that it is due to $\text{V}-\text{O}-\text{Si}$ stretching mode [20, 22, 28]. Intensity of Raman bands assigned to bulk oxide in Raman spectrum excited by 514.5 nm laser is strongly enhanced by resonance effect (light at 514.5 nm is absorbed by octahedrally coordinated bulk vanadium oxide clusters, see inset in Fig.4), therefore intensity of the V_2O_5 bands is much intensive than would be expected on the base of DR UV-vis spectra. The bands at ~ 483 , 603 and ~ 802 cm^{-1} have been assigned to the D1 and D2 defect mode of silica support, which have been attributed to tetracyclosiloxane rings produced via the condensation of surface hydroxyls, and the symmetrical $\text{Si}-\text{O}-\text{Si}$ stretching mode, respectively [52, 53]. Raman spectrum excited by UV laser is dominated by broad band at 487 cm^{-1} assigned to the D1 defect mode and band at 1024 cm^{-1} usually ascribed to $\text{V}=\text{O}$ stretching vibration. This band is about 16 cm^{-1} lower than that observed in the Raman spectrum excited by vis laser. Wu et al. attributed this difference in the frequencies to existence of two different $\text{V}=\text{O}$ stretching vibrations (each exhibited another resonance effect). This statement induces suggestion of presence of two types of VO_x species on silica support. For deeper investigation of this statement, we compared Raman spectra excited by UV and vis laser of samples with various distributions of vanadium complexes on the silica support (see Figure 5).

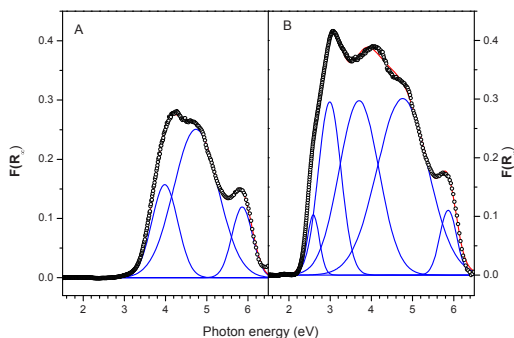


Figure 3 Deconvoluted DR UV-vis spectra of S-4 (A) and S-10 (B) samples. Black points are experimental data, red line is fitted envelope curve and blue lines are individual spectral bands.

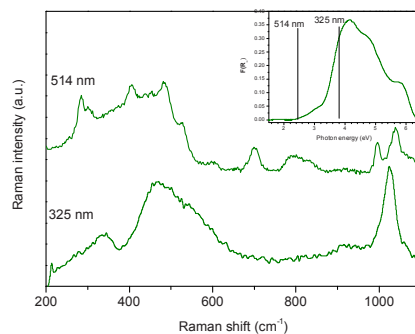


Figure 4 Raman spectra of dehydrated S-6 sample at 514.5 nm and 325 nm excitation. Inset: DR UV-vis spectrum of dehydrated S-6 sample with marked position of lights of individual lasers used for excitation of Raman spectra.

Raman spectra excited by vis laser of all investigated catalysts are depicted in the Figure 5A and B (plot A display whole spectral range from 200 to 1100 cm^{-1} and plot B display spectral features around

1000 cm^{-1} in more details). S-2 sample, which contain lowest amount of vanadia, exhibits only one band related to vanadia species at 1040 cm^{-1} . Intensity of this band is very low and band is relatively broad (full width at half maximum (FWHM) is 30 cm^{-1}). Band intensity increases with increasing vanadium loading, whereas position of band remains the same. Set of bands at 404, 697, and 993 cm^{-1} belonging to vibration of V_2O_5 crystallites start to evolve in the spectrum of S-4 sample in spite of absence bands at 2.6 or 3.1 eV in the DR UV-vis spectrum of this sample (cf. Fig. 1). This is due to extremely high sensitivity of Raman spectroscopy excited by 514.5 nm laser to the presence of oxide-like species caused by resonance effect. The bands of V_2O_5 increase in intensity with vanadium loading and dominate the spectra from 8 wt. % of vanadia. This is consistent with observed shift of absorption into visible region in DR UV-vis spectra of these samples. On the other hand, band at 1040 cm^{-1} is missing in the spectra of samples with concentration of vanadia 8 wt. % and higher. Broad shoulder of the band at 995 cm^{-1} at about 1023 cm^{-1} appears instead of band at 1040 cm^{-1} . This can be caused by relatively low amount of monomeric vanadium species in the high-loaded samples, whereas amount of oligomeric species simultaneously increases. This observation is in contradiction with observation on other supports. Changes in the coordination and extent of polymerization of the dehydrated surface VOx species on oxide supports as Al_2O_3 , ZrO_2 , TiO_2 or Nb_2O_5 are reflected by shift of this vibration band to slightly higher wavenumbers [3, 49]. Therefore, nature of this band is still not clear.

Raman spectra excited by UV laser are shown in the Figure 5 C and D. The spectra are dominated by broad band from silica support at 487 cm^{-1} except sharp band at 1025 cm^{-1} assigned to V=O vibration. Position of later band is invariable in spectra of all samples notwithstanding increasing vanadium loading and various populations of oligomeric species determined from UV-vis spectra. Intensity of this band is increasing only up to 6 wt. % of vanadia in the sample, then intensity decreases and new band at 993 cm^{-1} appears and rises with vanadium content. It is important to note that signal at 993 cm^{-1} , characteristic for vanadium oxide clusters, appeared as a very small shoulder in the Raman spectra excited by UV laser for samples with vanadium content 6 wt. % and for concentration of 8 wt.% becomes dominant, whereas presence of V_2O_5 clusters is evidenced in Raman spectra excited by vis laser (see Fig. 5A and B) for samples with vanadium content already 4 wt. %. On the other hand, the absorption bands at 2.6 and 3.1 eV characteristic for octahedrally coordinated oxide-like species was detected by DR UV-vis spectroscopy in the spectrum of sample with 6 wt.% (see Fig. 1). It is clear from this observation that the presence of even small amount of crystalline V_2O_5 can be more easily detected by Raman spectroscopy excited by vis laser than by UV laser. Comparison of Raman spectra excited by both 514.5 nm and 325 nm laser in the region of stretching vibrations of V=O band led to finding out that both spectra sets provide different picture. Band at 1025 cm^{-1} is present in all Raman spectra excited by UV laser and exhibits the same characteristic (FWHM is about 30 cm^{-1} as what as band at 1040 cm^{-1} in the Raman spectra excited by vis laser) in contrast to Raman spectra excited by vis laser in which band at 1027 cm^{-1} is detectable only in spectra of samples with the highest vanadium loading and its FWHM is significantly higher than FWHM of discussed band in Raman spectra excited by UV laser. Recent experimental and theoretical investigations [20-22] shown that bands at about 1020-1050 cm^{-1} can be ascribed to normal modes with substantial contribution of both V=O and in-phase V-O-Si vibrations. Therefore interpretation of bands and its intensity dependence on excitation is not simple.

From above reported data, it is clear that interpretation of Raman spectra is complicated and using of Raman spectroscopy for characterization of VOx species on silica surface is problematic. Dobler et al. state in their paper [22]: „Distinguishing between monomeric and polymeric sites by vibrational spectroscopy is hardly possible because the only difference is the occurrence of new bands in spectral region covered by other (support) band“. Based on DFT calculations [22], these additional bands are not caused by vibration of pure V-O-V bond but they are given by normal modes consisting of contribution

V-O-V (contribution to total (vibrational) energy defined by Dobler et al. [22] does not exceed 25 %), V=O and V-O-Si bonds and falling into spectral region $760\text{--}776\text{ cm}^{-1}$ for dimeric species and $840\text{--}870\text{ cm}^{-1}$ for tri- and tetrameric species. However, such bands were not detected in our spectra maybe due to their low intensity. Therefore presence/absence of particular band in the Raman spectrum cannot be clear indication of presence/absence of polymeric species. Raman spectroscopy is useful characterization technique for detection of presence of V_2O_5 microcrystallite, especially if suitable wavelength of laser is used for resonant enhancement of Raman intensity of bands. As we showed in our recent papers, DR UV-vis spectroscopy can provide more detailed information about nature and population of vanadium species on silica based supports. In addition, DR UV-vis spectra can be at least semi-quantitatively evaluated when diluted samples are used, whereas quantitative analysis of Raman spectra is difficult owing to different resonance effects and local nature of spectral information (Raman spectrometer is usually combined with microscopy and spectrum is collected from relatively small area of sample).

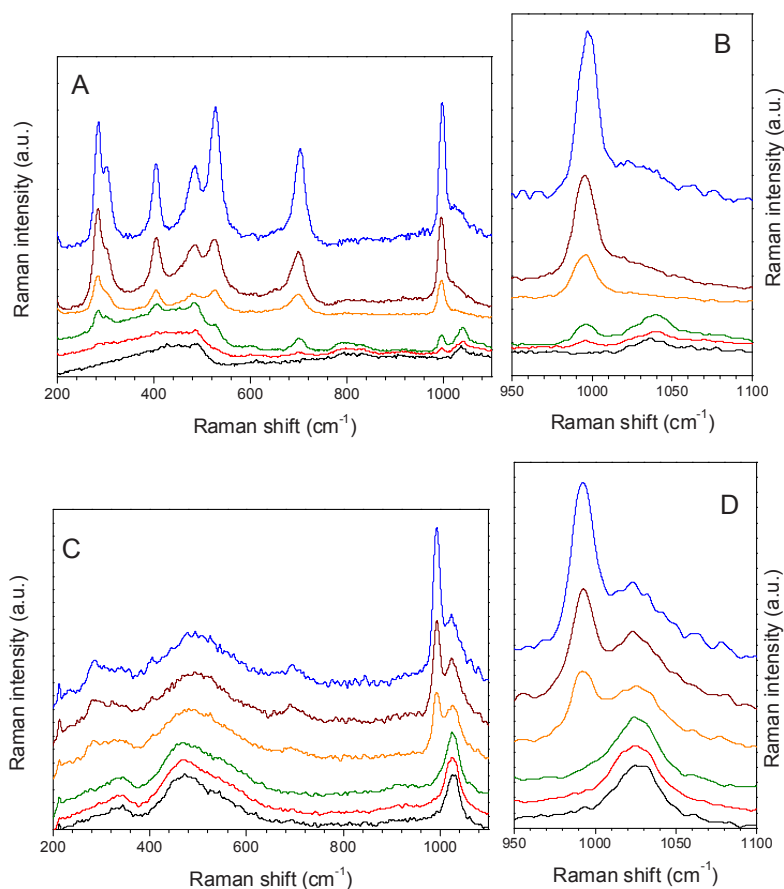


Figure 5 Raman spectra excited by visible (A and B) and UV (C and D) laser of dehydrated samples under study. Left panels depict full range of spectra, right panels display detail of spectral range of stretching vibrations around 1000 cm^{-1} . For assignment of individual curves to individual samples see Table 1. Spectra in panel C and D were normalized to the intensity of 480 cm^{-1} band.

4. Conclusion

Comparison of DR UV-vis spectra obtained on wide set of VO_x-HMS samples differing in vanadium content in wide range and population of individual vanadium species with Raman spectra excited by vis and UV lasers clearly showed suitability of UV-vis spectroscopy for characterization of vanadium species spread on silica support. On the other hand, Raman spectroscopy is very sensitive technique for monitoring of V₂O₅ oxide presence. Using of several excitation wavelengths is recommended for characterization of dispersed vanadium complexes by Raman spectroscopy. It enables selective resonance enhancement that can be used for distinguishing different species.

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