Adsorption (2013) 19:339–347
DOI 10.1007/s10450-012-9456-5

CO and NO adsorption on VO_x/SBA-15 catalysts: an FT-IR spectroscopic study

R. Bulánek · N. Drenchev · P. Čičmanec · M. Setnička

Received: 1 November 2012 / Accepted: 7 December 2012 / Published online: 21 December 2012

Abstract The adsorption of CO and NO over VO_x-SBA-15 mesoporous materials with different vanadium content was investigated by FT-IR spectroscopy. Vanadium complexes were reduced in situ by hydrogen atmosphere at 450 °C for 3 h. Spectra of reduced samples show increasing in intensity of silanol groups, caused by dissociation of V–O(Si) bonds and formation of new H–O(Si) bonds. Reduction occurs with formation of water. The band corresponds to overtone of V=O stretching modes decreases in intensity because of oxygen withdrawing from V=O species.

Presence of V^{4+} and V^{3+} species was observed. Inspection of CO adsorbed IR spectra evidenced existence at least two different type of V^{3+}–CO complexes on the silica surface differing in both stretching frequencies and complex stabilities. We did not found principal difference between spectra of absorbed CO at −196 °C on the samples with different concentration of vanadium, probably because of relative low degree of reduction. As well as heterogeneity of surface V^{3+} and V^{4+} species was evidenced by adsorption of NO. Both V^{3+} and V^{4+} ions possess two effective coordinative vacancies and as a result can adsorb two NO molecules forming dinitrosyls. A part of V^{3+} cations forms only mononitrosyls characterize by band at 1724 cm^{-1}. Results obtained after NO adsorption reveal existence of three different kinds of vanadium species. Probably two of them are isolated and associated vanadium sites. The third type of vanadium has different surrounding than other two types. It was demonstrated that NO is a better probe than CO for testing the oxidation and coordination state of reduced vanadium species.

Keywords Vanadium · SBA-15 · FT-IR · Carbonyls · Nitrosyls

1 Introduction

Ordered mesoporous SBA-15 silicas, with uniform pores size distribution and high surface area, are interesting supports for vanadium-based catalysts with plenty of accessible, isolated and well-defined active sites (Cavani et al. 2007). VO_x-SBA-15 catalyst exhibits high selectivity to olefins at high propane conversions in the oxidative dehydrogenation of propane (Bulanek et al. 2012b; Dinse et al. 2009; Hess 2007; Liu et al. 2004). However, a fundamental understanding of the nature and redox properties of the vanadium species anchored on the surface of the SBA-15 support remained to be established. 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, UV-vis diffuse reflectance (DR), solid-state ^{51}V NMR, ESR, etc.) (Tian et al. 2006; Venkov et al. 2007; Bulanek et al. 2011; Deo et al. 1994). Despite major efforts to examine the structure of surface vanadia complexes on dehydrated VO_x-silica materials, mainly using Raman spectroscopy, no decisive picture has been obtained so far. It is generally accepted that, at very low vanadia loadings the surface vanadium oxide species are isolated tetrahedrally coordinated VO_4 units. However, increasing vanadia loading on the surface leads to polymerization of surface vanadyls even to bulk vanadium pentoxide. Existence of oligomeric V–O–V species on the VO_x-silica materials with medium vanadium loading is still

---

R. Bulánek · N. Drenchev (✉) · P. Čičmanec · M. Setnička
Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic
e-mail: ndrenchev@svr.igic.bas.bg

under debate. In recent IR study of interaction of CO with VO_x-SBA-15 containing 2.7 wt% of V, formation of two different type of carbonyls on reduced sample was observed and ascribed by authors to the presence of VO_x isolated and associated species on the surface (Venkov et al. 2007). In our previous works we distinguished various vanadium species differing in degree of polymerization/condensation by DR UV-vis spectroscopy (Bulanek et al. 2011) and shown on the wide set of VO_x/HMS materials that they differ substantially in activity and selectivity in ODH reaction and this difference also depend on the type of raw alkane (Bulanek et al. 2012a; Setnicka et al. 2011). It can be ascribed to the differences in the redox properties of individual vanadium complexes. Unfortunately, deeper investigation of redox properties by DR UV-vis spectroscopy is not easy due to strong overlapping of charge transfer signals arising from different oxidation states of vanadium. Much more convenient spectroscopic technique seems to be FT-IR spectroscopy of suitable probe molecules. Therefore, we report IR study of CO and NO adsorption as probe molecules to determine the oxidation and coordination state of vanadium after reduction by H_2 at 450 °C for 3 h. We compared our results with results obtained previously by Venkov et al. (2007) over silica with low concentration of vanadium. In addition, experimental data obtained over samples differing in vanadium content are compared and discussed.

2 Experimental

2.1 Materials

Purely siliceous SBA-15 mesoporous molecular sieve were synthesized as reported earlier (Zukal et al. 2008) using a triblock copolymer, Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BASF/Aldrich) as a structure directing agent. TEOS was used as a silica precursor yielding a typical synthesis molar ratio TEOS:HCl:P123:H_2O = 1:6.2:0.017:197. The synthesis mixture was vigorously stirred at 35 °C for 5 min and subsequently aged under static conditions for 24 hours at 35 °C and 48 hours at 97 °C. The resulting solid was recovered by filtration, extensively washed out with distilled water and ethanol, and dried at 100 °C overnight. The template was removed by calcination in a stream 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/H_2O 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. The same catalysts we have used in our previous paper (Bulanek et al. 2012b), where more characterization details is reported. Carbon monoxide (>99.997) and nitric oxide (>99.5) were supplied by Linde AG.

2.2 Instrumental methods

Physico/chemical characterization is published in more details in previous work (Bulanek et al. 2012b). Self-supporting wafers (ca. 5–8 mg/cm^{-2}) were prepared from the sample powder and treated directly into glass IR cell. The cell was connected to a vacuum-adsorption apparatus with residual pressure of 10^{-3} mbar. Prior to the adsorption measurements, the samples were activated by heating from ambient temperature to 450 °C for 1 h and 1 h evacuation at the same temperature. The samples were oxidized by O_2 at 450 °C for 20 min before reduction and then evacuated for 30 min. The samples were reduced by treatment with hydrogen (400 mbar) at 450 °C for 3 h. After reduction, samples were evacuated for 1 h at the reduction temperature. Before adsorption, carbon monoxide was purified by liquid nitrogen trap while NO was additionally purified by fraction distillation. The FT-IR spectra of CO and NO molecules adsorbed on the VO_x species were recorded at liquid nitrogen and room temperature, respectively, for decreasing surface coverage due to evacuation using FT-IR Nicolet 6700 spectrometer (equipped with MCT detector) at a spectral resolution of 2 cm^{-1} and accumulating of 64 scans. Spectra obtained through subtraction of the spectrum of the treated sample in vacuum from the spectrum in presence of the probe molecules are reported here. The spectra are gas phase corrected.

3 Results and discussion

Spectra of activated samples are presented on Figs. 1 and 2. In the region of (O–H) stretching modes, the IR spectrum

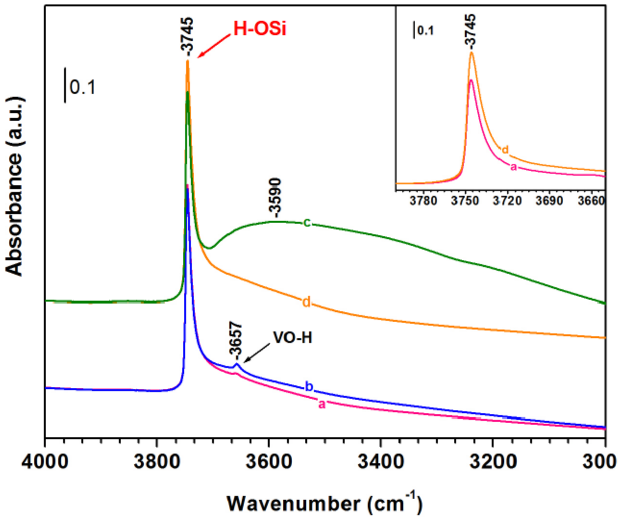

Fig. 1 FT-IR spectra of V-SBA-15 containing 3.6 wt% of V after oxidation and evacuation (*a*), after introduction of H_2 (400 mbar) (*b*), after reduction at 450 °C before evacuation (*c*) and after evacuation at 450 °C (*d*)

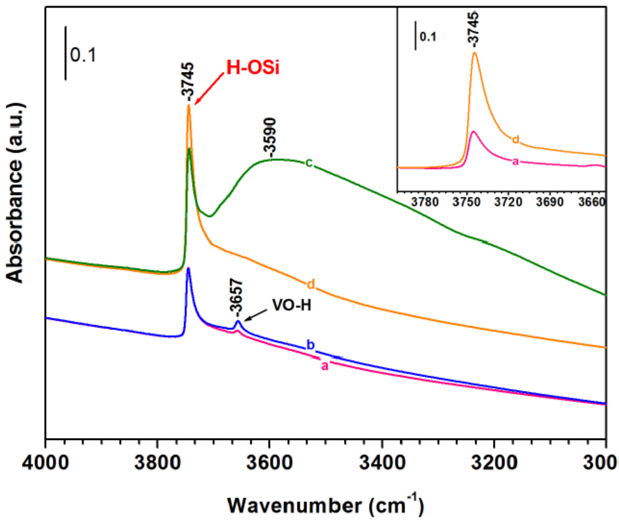

Fig. 2 FT-IR spectra of V-SBA-15 containing 9 wt% of V after oxidation and evacuation (*a*), after introduction of H_2 (400 mbar) (*b*), after reduction at 450 °C before evacuation (*c*) and after evacuation at 450 °C (*d*)

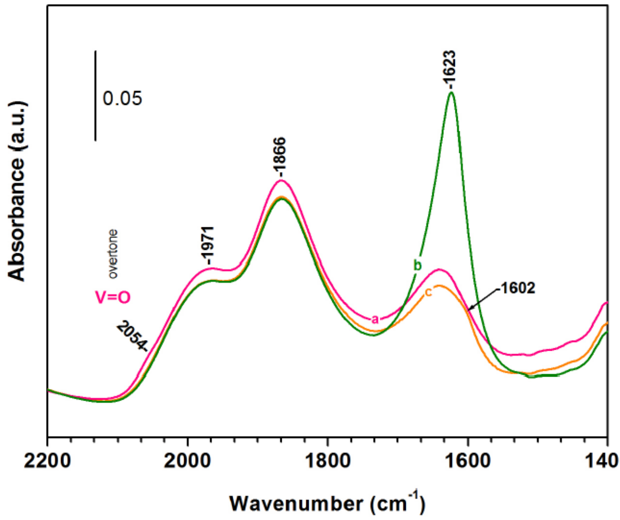

Fig. 3 FT-IR spectra of V-SBA-15 containing 3.6 wt% of V after oxidation and evacuation (*a*), after reduction at 450 °C before evacuation (*b*) and after evacuation at 450 °C (*c*)

of activated samples exhibits an intense band at 3745 cm^{-1} due to silanol groups (Zarubin 2001; Boehm and Knozinger 1983). Silanol band decreases in intensity with increasing content of vanadium from 3.6 wt% to 9 wt% (see spectrum a Figs. 1 and 2). According to the literature data the band at 3657 cm^{-1} is ascribed to VO-H stretching modes (Tielens et al. 2009; Berndt et al. 2000; Martra et al. 2000; Schramlmarth et al. 1991; VanDerVoort et al. 1997; Nguyen et al. 2006). At lower frequencies, bands at 1971, 1866 and 1623 cm^{-1} were registered. These bands were attributed to the overtones and combination modes of the SBA-15 skeletal vibrations (Figs. 3 and 4) (Boehm and Knozinger 1983).

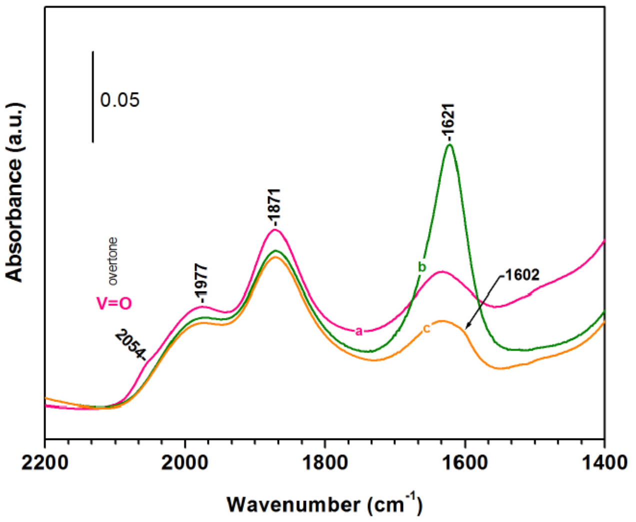

Fig. 4 FT-IR spectra of V-SBA-15 containing 9 wt% of V after oxidation and evacuation (*a*), after reduction at 450 °C before evacuation (*b*) and after evacuation at 450 °C (*c*)

The low intensity band at 2054 cm^{-1} is due to overtones of V=O stretching modes (1020 cm^{-1}) (Kantcheva et al. 1992; Concepcion et al. 1999). It's intensity increases with increasing concentration of vanadium (cf. spectra denoted a in Figs. 3 and 4). The band at 1020–1027 cm^{-1} is superimposed with the skeletal vibration of SBA-framework and is, therefore, not usable for analysis. Reduction of the samples by H_2 leads to alterations in spectra of the samples. The main changes in the spectra are:

- New band at 1602 cm^{-1} was observed.
- The band of silanol groups at 3745 cm^{-1} was increased in intensity.
- The band corresponds to overtone of V=O stretching modes was decreased in intensity.

After oxidation of the samples the band at 1602 cm^{-1} disappears from the spectra. Probably different bonding of vanadium after reduction on the surface of the SBA-15 leads to the appearance of this band. The band of silanol groups increases in intensity caused by dissociation of V–O(Si) bonds and formation of new H–O(Si) bonds (inset of Figs. 3 and 4). The band corresponds to overtones of V=O decreases in intensity because of oxygen withdrawing from V=O species accompanied by formation of water (bands at 3590 cm^{-1} and 1623 cm^{-1}).

3.1 Adsorption of CO on pure SBA-15 sample

Low-temperature adsorption of CO on pure SBA-15 samples leads to the appearance of four bands with maxima at 2157, 2138, 2134 and 2110 cm^{-1} (Fig. 5). Simultaneously with the formation of these bands, the band of silanol groups at 3747–3750 cm^{-1} decreases in intensity and a new band

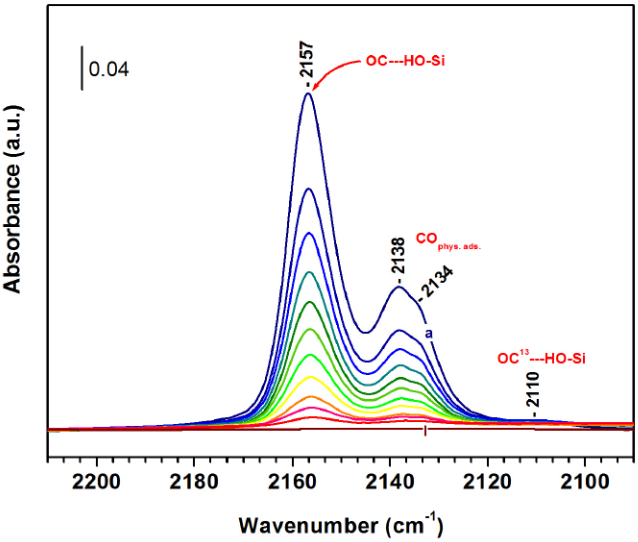

Fig. 5 FT-IR spectra of CO adsorbed at −196 °C on SBA-15. Equilibrium CO pressure of 1.90 mbar and evolution of the spectra during short evacuation (*a*–*l*). The spectra are background corrected

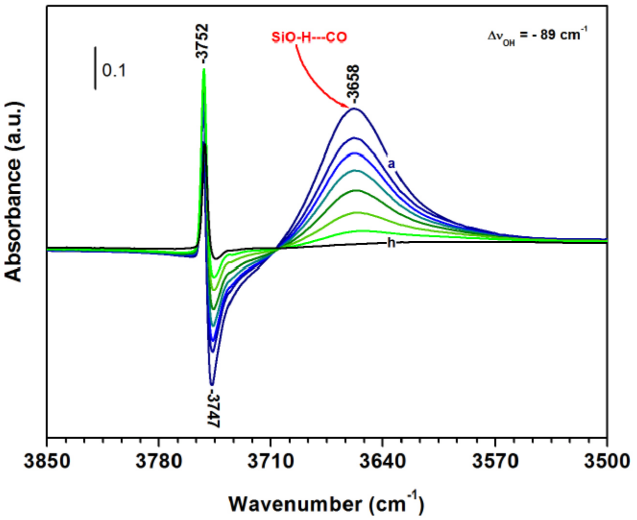

Fig. 6 FT-IR spectra of silanol groups after CO adsorption at −196 °C on SBA-15. Equilibrium CO pressure of 1.9 mbar and evolution of the spectra during short evacuation (*a*–*h*). The spectra are background corrected

with a maximum at 3658 cm^{-1} forms in the spectrum (Fig. 6 spectrum a). This band is due to SiO-H—CO stretching modes (stretching frequency shift is $\Delta\nu = -89$ cm^{-1}). The band at 2157 cm^{-1} is ascribed to H-bonded CO with silanol groups. The bands at 2138, 2134, and 2110 cm^{-1} are assigned to physically adsorbed CO and H-bonded ^{13}CO (natural occurrence of ^{13}CO is about 1 %), respectively (Hadjiivanov and Vayssilov 2002).

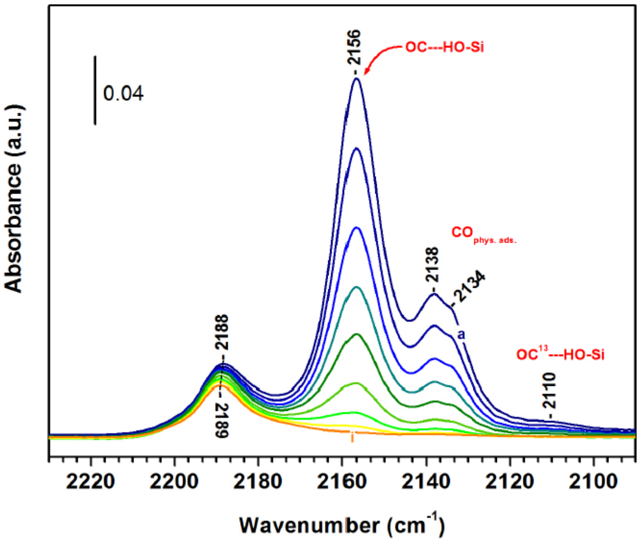

Fig. 7 FT-IR spectra of CO adsorbed at −196 °C on V-SBA-15 with 3.6 wt% of V. Equilibrium CO pressure of 1.8 mbar and evolution of the spectra during short evacuation (*a*–*i*). The spectra are background corrected

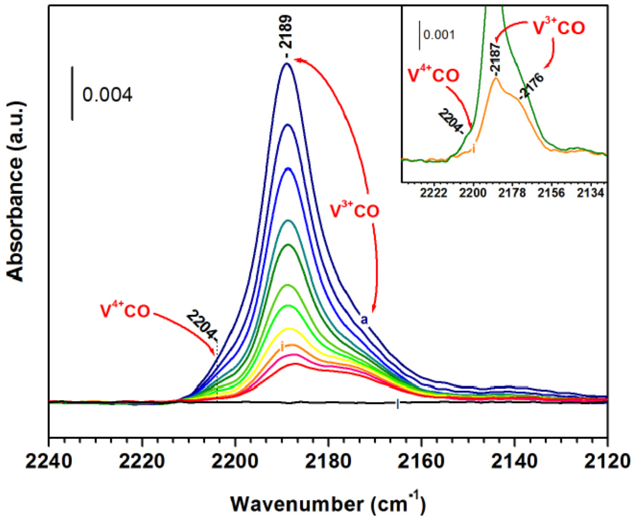

Fig. 8 FT-IR spectra of CO adsorbed at −196 °C on V-SBA-15 with 3.6 wt% of V. Evolution of the spectra during evacuation at −196 °C (*a*–*i*) and increasing the temperature from −196 °C to RT (*i*–*l*). The spectra are background corrected

3.2 Adsorption of CO on reduced V-SBA-15 samples

Adsorption of CO at low-temperature on reduced V-SBA-15 samples provokes formation of a new band at 2189 cm^{-1} (Figs. 7, 8, 9 and 10). The other four bands with maxima at 2156, 2138, 2134 and 2110 cm^{-1} were discussed previously (see above). Upon evacuation at low temperature all bands start to decrease in intensity. The band at 2188 cm^{-1} is the most stable to evacuation and was assigned to carbonyls of vanadium (Hadjiivanov and Vayssilov 2002; Concepcion et al. 1999; Davydov 1993; Gerasimov and Filimonov 1981;

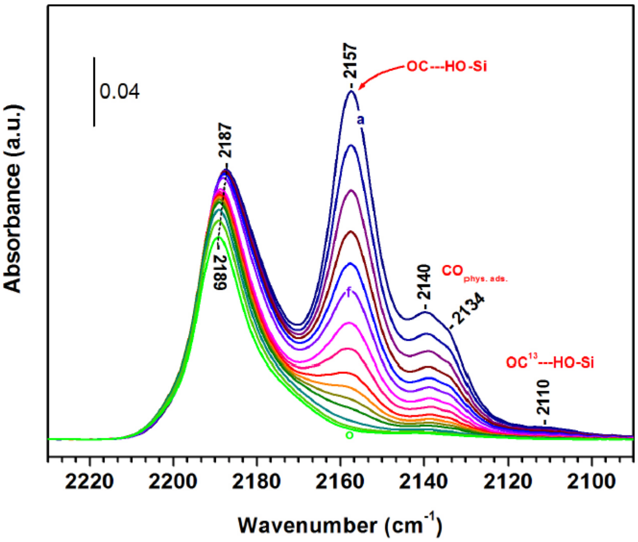

Fig. 9 FT-IR spectra of CO adsorbed at −196 °C on V-SBA-15 containing 9 wt% of V. Equilibrium CO pressure of 1.95 mbar and evolution of the spectra during short evacuation (*a*–*f*) and at condition of dynamic vacuum (*g*–*o*).The spectra are gas phase and background corrected

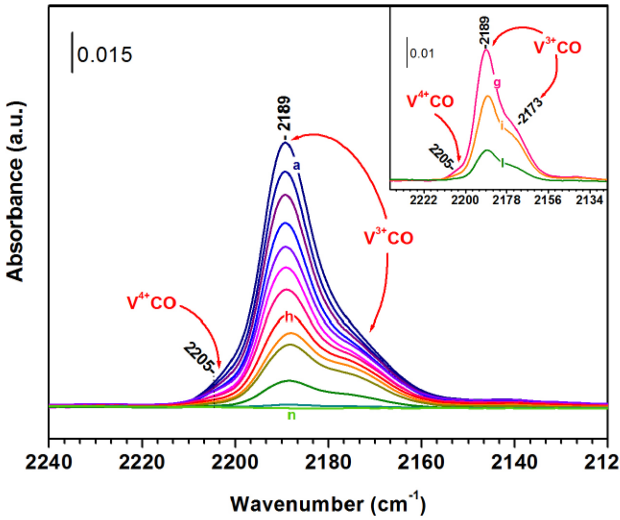

Fig. 10 FT-IR spectra of CO adsorbed at −196 °C on V-SBA-15 containing 9 wt% of V. Evolution of the spectra during evacuation at −196 °C (*a*–*h*) and increasing the temperature from −196 °C to RT (*i*–*n*). The spectra are background and gas phase corrected

Jonson et al. 1988a, 1988b). These carbonyls are not stable during evacuation at room temperature, contrary to observation by Venkov et al. (2007). This band is blue shifted with decreasing of coverage for both samples (Fig. 7 and Fig. 9). This trend could be explained with the so-called static effect, which is typical for oxide-supported systems and indicates that a fraction of vanadium atoms are associated (Hadjiivanov and Vayssilov 2002). At low coverage the band at 2189 cm^{-1} consists of three components with maxima at around 2205, 2189 and 2176 cm^{-1} for both samples (Fig. 8 and Fig. 10). The band at 2205 cm^{-1} was assigned to V^{4+}–CO species (Hadjiivanov and Vayssilov 2002; Concepcion et al. 1999; Davydov 1993). The other two bands were ascribed to two different types of vanadium species with different electrophilicity (Davydov 1993; Jonson et al. 1988a; Ivanova et al. 2006). The species of V^{3+} at lower wavenumber are slightly more stable during evacuation. There are several possibility causes for this different electrophilicity. One of them is that in the channels of SBA-15 there are (i) isolated and (ii) associate vanadium sites. In this light, Jonson et al. (1988b) have reported that with increasing vanadium content the position of the main band of V^{3+}–CO carbonyls is blue-shifted. After adsorption of CO on reduced V/SiO$_2$ (0.1 wt% V) they found a band at 2183 cm^{-1}, while for V/SiO$_2$ (2 wt% V) the band appeared at 2187 cm^{-1}. In the paper of Venkov et al. (2007), the band maximum was registered at 2189 cm^{-1} for V-SBA-15 with 2.7 wt% of vanadium. Hence on results obtained by Jonson et al. (1988b) and their results Venkov et al. (2007) suggested that vanadium site in the matrix of SBA-15 are partly associated. We observed bands with maxima at 2188 and 2187 cm^{-1} for the sample containing 3.6 wt% and 9 wt% of vanadium, respectively. The area of the band at 2188 cm^{-1} is apparently higher for the sample with 9 % (Fig. 9) of vanadium than the area of the same peak for sample with 3.6 % of vanadium (Fig. 7). Hence, we evidently created more reduced V^{3+} species in the sample with 9 % than in the sample with 3.6 % and no dependence between the concentration of vanadium and position of this band can be found.

Another possible reason for heterogeneity of the vanadium sites is that one of these sites is bound to isolated hydroxyl groups. In this case a part of vanadium sites are characterized by different surroundings, which could explain the difference in their electrophilicity. However after reduction and evacuation of the samples we did not observe bands of HO groups connected to vanadium. These bands with maxima at 3657 cm^{-1} present in the spectra of the samples after oxidation and evacuation where vanadium exists in +5 oxidation state.

The third possible reason is presence of different kinds of silanol groups: (i) isolated, (ii) geminal, and (iii) vicinal hydroxyl groups (Boehm and Knozinger 1983; Boehm 1966). Hence, one would expect the carbonyl complexes of vanadium ions located on isolated and geminal (Si(OH)$_2$) silanol groups to have slightly different frequencies (Shenderovich et al. 2003). Spectra of our samples show only isolated and H-bonded silanol groups.

Nowadays the most acknowledged theory expects the existence of three different types of vanadium oxide species on the surface (Tian et al. 2006; Kung 1994; Blasco and Nieto 1997; Keller et al. 2006): (i) the isolated monomeric tetrahedrally coordinated VO$_4$ species linked by three V–O-support bonds to support at dehydrated state, (ii) the

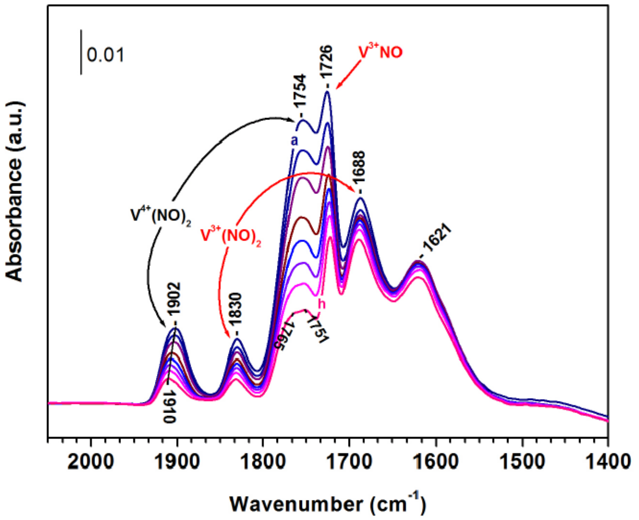

Fig. 11 FT-IR spectra of NO (1.25 mbar equilibrium pressure) adsorbed at RT on V-SBA-15 containing 3.6 wt% of V. Evolution of the spectra during evacuation at room temperature (*a*–*h*). Spectrum (*a*) was collected 50 min after introduction of NO. The spectra are background corrected

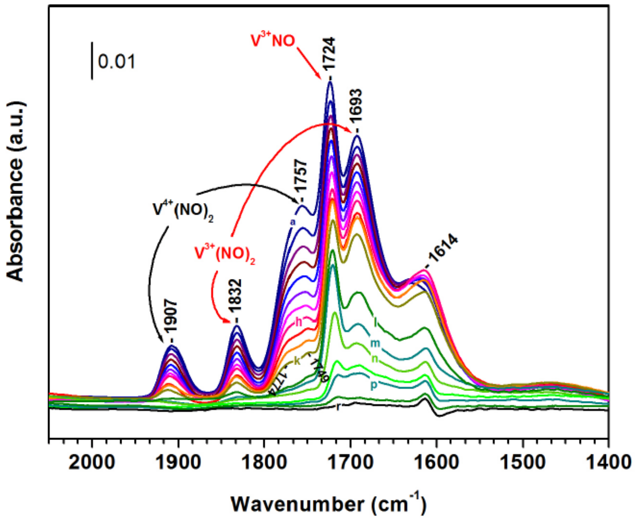

Fig. 12 FT-IR spectra of NO (0.8 mbar equilibrium pressure) adsorbed at RT on V-SBA-15 containing 9 wt% of V. Evolution of the spectra during evacuation at room temperature (*a*–*h*), at 50 °C for 3, 5 and 10 min (*i*–*k*), at 80 °C 3 min (*l*), at 100 °C 3 min (*m*), at 110 °C 5, 10 and 10 min (*n*–*p*) and at 150 °C 5 and 10 min (*q*–*r*). The spectra are background corrected

oligomeric/polymeric VO_x species of distorted tetrahedral symmetry bonded by bridging V–O–V bonds to other units, and (iii) 2D/3D crystalline V_2O_5 nanoparticles (NPs). Some authors mentioned as fourth (iv) type the mixed oxide compounds or solid solution with some oxide supports at elevated temperatures (e.g., $AlVO_4$, $V_xTi_{1-x}O_2$) on the surface (Tian et al. 2006).

Let us mention that after reduction surrounding of vanadium is changed because of oxygen withdrawing from V=O species attendance by formation of water and dissociation of V–OSi bonds. Oxygen needed for formation of water may become from V–O–V species (Ferreira and Volpe 2002). It is reasonably to propose different ratio between structures (i), (ii) and (iii) after reduction compare this ratio when samples are oxidized. On the other hand, reduction of different structures (monomeric and 2D/3D crystalline V_2O_5 nanoparticles) takes place with different rate, because the maxima of their reduction peaks in TPR experiments shifts in temperature as the different species appears on the surface of the support (Setnicka et al. 2011). The results of the XPS analysis of V_xO_y/SBA-15 after H_2 treatment at 415 °C for 1 h obtained by Venkov et al. (2007) shows 50.3 % of V^{3+}.

3.3 Adsorption of NO on reduced sample at room temperature

For deeper insight into character of heterogeneity of reduced vanadium species adsorption of NO was carried out. NO is suitable probe molecules due to better distinguish of V^{4+} and V^{3+} complexes. Adsorption of NO on reduced samples leads to the appearance of a series of bands with maxima at 1902, 1830, 1754, 1726, 1688 and 1621 (Figs. 11 and 12). It is well known that both V^{4+} and V^{3+} cations form dinitrosyl species characterized by asymmetric and symmetric vibrations. The $V^{4+}(NO)_2$ complexes display ν_s at 1920–1880 cm^{-1} and ν_{as} at 1785–1753 cm^{-1} (Ivanova et al. 2006; Hadjiivanov and Vayssilov 2002; Hadjiivanov 2000). The ν_s modes for $V^{3+}(NO)_2$ are observed at 1835–1822 cm^{-1} and the respective asymmetric modes, at 1705–1685 cm^{-1}. Evacuation at ambient temperature (Fig. 11 and spectra a–h Fig. 12) provokes decreasing in intensity of $V^{4+}(NO)_2$ and $V^{3+}(NO)_2$ complexes. The bands at 1621 cm^{-1} and 1614 cm^{-1} remain relatively stable upon evacuation at ambient temperature. These bands were assigned to nitro (Venkov et al. 2007; Hess 2009) or nitrato compounds (Ivanova et al. 2006). Let us take a look on spectrum *f* on Fig. 12. The intensities of the bands at 1907 cm^{-1} and 1757 cm^{-1} ($V^{4+}(NO)_2$ complexes) are half of their initial intensity. The intensities of the bands characterizing ν_s and ν_{as} modes of $V^{3+}(NO)_2$ complexes have different behavior. Intensity of the band at 1832 cm^{-1} is half of initial intensity but intensity of the band at 1693 cm^{-1} remains 82 % of its initial intensity. Similar behavior in the spectra was observe for the sample with 3.6 wt% of V. This phenomenon was observed previously by Ivanova et al. (2006) and can be explained by a larger angle between the NO molecules at low coverage. The band at 1754 cm^{-1} was split at low coverage in two component with maxima at 1765 and 1751 cm^{-1}. The same splitting was observed in the spectra of the sample containing 9 wt% of V (Fig. 12). The bands at 1902 cm^{-1} and 1907 cm^{-1} also consisting of two components, but the splitting being very low (∼2 cm^{-1}). This splitting of the band was observed by Venkov et al. (2007)

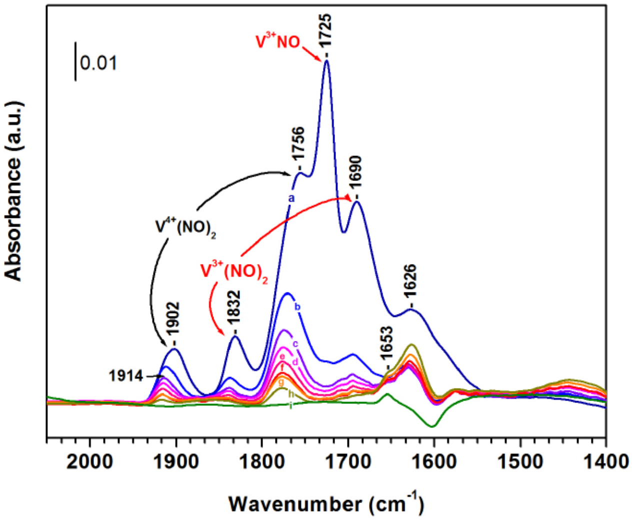

Fig. 13 FT-IR spectra of NO (0.8 mbar equilibrium pressure) adsorbed at RT on reduced V-SBA-15 containing 3.6 wt% of V (*a*), addition of O_2 (7 mbar) at RT (*b*), development of the spectra with time (*c*–*e*), increasing the amount of O_2 to 20 mbar (*f*), 50 mbar (*g*) and 156 mbar (*h*) and after evacuation at 200 °C for 5 min (*i*). The spectra are background corrected

on V-SBA-15 and Ivanova et al. (2006) on VSiBEA. The authors suggested the existence of two types of $V^{4+}(NO)_2$ dinitrosyls. In our work we were observed a new band at 1726 cm^{-1}. We will debate behavior of this band later. In conclusion we can say that both samples contain the same or very similar species of vanadium.

3.4 NO and O_2 co-adsorption on reduced sample (3.6 wt% V)

In order to obtain information on the reactivity of the nitrosyls species, we studied their interaction with O_2. The sample was reduced again at 450 °C by H_2 and initially NO (0.8 mbar equilibrium pressure) was adsorbed on it. The same species of vanadium nitrosyls were observed in the spectra (Fig. 13 spectrum a). After addition of O_2 (7 mbar) all bands decrease in intensity and their maxima are blueshifted. The band at 1725 cm^{-1} dramatically decreases in intensity and almost disappears from spectrum. This fact indicates that this band is associated with individual compound which is very reactive and oxidize easier compare to $V^{3+}(NO)_2$ complexes. Taking into account frequency, stability and behavior of the band after NO and O_2 co-adsorption we assigned it to $V^{3+}NO$ (Gerasimov and Filimonov 1984). The evolution of the spectra with time shows that the bands due to ν_s and ν_{as} of $V^{3+}(NO)_2$ decrease in intensity and disappear much faster than the bands of the respective $V^{4+}(NO)_2$ species.

The band at 1626 cm^{-1} starts to decrease in intensity and new bands at 1630 cm^{-1} and 1653 cm^{-1} appears in the spectra. Venkov at al. assigned the band at 1620 cm^{-1} to the $\nu_{as}(NO_2)$ stretching modes of nitro compounds of V^{+5}. In their work they observed two bands at 1639 cm^{-1} and 1573 cm^{-1} raised after NO and O_2 co-adsorption and ascribed them to bridging and bidendate nitrates of vanadium in oxidation state +5. As we mentioned the ratio between monomeric and associated species was changed after reduction. In any cases concentration of bridging vanadium species is lower compare to monomeric. For that reason, intensity of the band corresponding to bridging nitrates has to be less intense than the band of bidendate nitrates but it is not observed in the spectra obtained by Venkov et al. In our case we did not observed band at 1573 cm^{-1} in the spectra of the samples. One possible explanation of that observation is that bridging nitrates generate not only on V–O–V species. If monomeric vanadium sites are close to each other, they may form bridging nitrates too. The results obtained by Venkov et al. (V_xO_y/SBA-15) (Venkov et al. 2007), Ivanova et al. (VSiBEA) (Ivanova et al. 2006) and Hadjiivanov et al. (VO_x/TiO_2) (Hadjiivanov et al. 2000) after adsorption of NO and introducing of O_2 has shown formation of nitrates bands at 1639 cm^{-1}, 1633 cm^{-1} and 1622 cm^{-1} respectively. These bands were increased in intensity with time and pressure of oxygen and had higher intensity compared to the intensity of the band at around 1900 cm^{-1} characterizing ν_s of $V^{4+}(NO)_2$ complexes. Vanadium in +5 oxidation state does not form nitrates. Nitrates form only on V^{+3} and V^{+4} species. After co-adsorption of NO and O_2 on oxidized V-SBA-15 containing 9 wt% of vanadium we did not observed bands of nitrates on the surface. It is well known that mixture of NO and O_2 is a strong oxidizer therefore we ascribe the bands at 1630 cm^{-1} and 1653 cm^{-1} to two different kind of nitrates which may form on vanadium in the same or different oxidation state. The band at 1653 cm^{-1} remains in the spectrum upon evacuation at 200 °C for 5 min while the band at 1630 cm^{-1} disappears in the spectrum. The frequency of the band at 1626 cm^{-1} is too high for nitro compound of vanadium and in our case has relatively high intensity. Topsoe et al. (1995) observed doublet band centered at 1617 cm^{-1} of adsorbed NO_2 on V_2O_5/TiO_2. We can speculate that the band at 1626 cm^{-1} corresponds to nitrates of V^{3+} or V^{4+}, V^{n+} NO_2 complexes or both. Presence of water on the surface of the sample will lead to the appearance of the band at the same position. Probably in 1630–1614 cm^{-1} region we observed overlapping of the bands of different compounds. As ionic compounds nitrates has a higher thermal stability compared to NO_2 complexes. Their thermal stability depends on the structure and on the kind of the cation to which they are bonded. If we accepted that this band is caused by nitrates of V^{3+} then after introduction of O_2 vanadium will oxidize to +5 (which form does not generate nitrates) and intensity of the band at 1626 cm^{-1} will start to decrease. The new bands in the spectra with maxima at 1630 cm^{-1} and 1653 cm^{-1} should be caused by nitrates of V^{4+}. The same effect will be observed if NO_2 complexes are formed on V^{3+} and V^{4+}.

4 Conclusions

Carbonyls and nitrosyls of vanadium on fully oxidized sample are not observed because of covalent character of the V–O bonds and coordinative saturation of V^{+5} cations. Different oxidation states (V^{+4} and V^{+3}) and two different species of V^{3+} are established after CO adsorption at −196 °C. We did not found principal difference between spectra of absorbed CO at −196 °C on the samples with different concentration of vanadium. This can be caused by relative low degree of reduction obtained after reduction in hydrogen atmosphere of 400 mbar at 450 °C for 3 h.

Analysis of the spectra obtained led to conclusion that the main part of reduced V atoms are in +3 oxidation state. Spectra of reduced samples show increasing in intensity of silanol groups, caused by dissociation of V–O(Si) bonds and formation of new H–O(Si) bonds. Reduction occurs with formation of water. The band corresponds to overtone of V=O stretching modes decreases in intensity because of oxygen withdrawing from V=O species.

Different oxidation states (V^{+4} and V^{+3}) and two different species of V^{4+} and V^{3+} are established after NO adsorption at ambient temperature. A part of V^{3+} cations forms only mononitrosyls characterized by band at 1724 cm^{-1} whereas other part of V^{3+} cations is able to bind two NO.

Results obtained after NO adsorption reveal existence of three different kinds of vanadium species. Probably two of them are isolated and associated vanadium sites. The third type of vanadium has different surrounding than other two types. It was demonstrated that NO is a better probe than CO for testing the oxidation and coordination state of reduced vanadium species.

Acknowledgements This work was supported by the Czech Science Foundation under project P106/10/0196 and The Ministry of Education, Youth and Sports of the Czech Republic project CZ.1.07/2.3.00/30.0021 “Strengthening of Research and Development Teams at the University of Pardubice”.

References

Berndt, H., Martin, A., Bruckner, A., Schreier, E., Muller, D., Kosslick, H., Wolf, G.U., Lucke, B.: Structure and catalytic properties of VOx/MCM materials for the partial oxidation of methane to formaldehyde. J. Catal. **191**(2), 384–400 (2000)

Blasco, T., Nieto, J.M.L.: Oxidative dehydrogenation of short chain alkanes on supported vanadium oxide catalysts. Appl. Catal. A, Gen. **157**(1–2), 117–142 (1997)

Boehm, H., Knozinger, H.: Nature and Estimation of Functional Groups on Solid Surfaces. Catalysis Science and Technology, vol. 4. Springer, New York (1983)

Boehm, H.P.: Functional groups on surfaces of solids. Angew. Chem., Int. Ed. Engl. **5**(6), 533 (1966). doi:10.1002/anie.196605331

Bulanek, R., Capek, L., Setnicka, M., Cicmanec, P.: DR UV-vis study of the supported vanadium oxide catalysts. J. Phys. Chem. C **115**(25), 12430–12438 (2011). doi:10.1021/jp112206c

Bulanek, R., Cicmanec, P., Sheng-Yang, H., Knotek, P., Capek, L., Setnicka, M.: Effect of preparation method on nature and distribution ofvanadium species in vanadium-based hexagonal mesoporous silica catalysts:impact on catalytic behavior in propane ODH. Appl. Catal. A, Gen. **415**, 29–39 (2012a). doi:10.1016/j.apcata.2011.11.033

Bulanek, R., Kaluzova, A., Setnicka, M., Zukal, A., Cicmanec, P., Mayerova, J.: Study of vanadium based mesoporous silicas for oxidative dehydrogenation of propane and n-butane. Catal. Today **179**(1), 149–158 (2012b). doi:10.1016/j.cattod.2011.08.044

Cavani, F., Ballarini, N., Cericola, A.: Oxidative dehydrogenation of ethane and propane: how far from commercial implementation? Catal. Today **127**(1–4), 113–131 (2007)

Concepcion, P., Hadjiivanov, K., Knozinger, H.: Low-temperature CO adsorption on v-containing aluminophosphates: an FTIR study. J. Catal. **184**(1), 172–179 (1999)

Davydov, A.A.: A study of vanadium-oxide compositions on supports by optical spectroscopy. Kinet. Catal. **34**(6), 951–961 (1993)

Deo, G., Wachs, I.E., Haber, J.: Supported vanadium-oxide catalysts-molecular structural characterization and reactivity properties. Crit. Rev. Surf. Chem. **4**(3–4), 141–187 (1994)

Dinse, A., Khennache, S., Frank, B., Hess, C., Herbert, R., Wrabetz, S., Schlogl, R., Schomacker, R.: Oxidative dehydrogenation of propane on silica (SBA-15) supported vanadia catalysts: a kinetic investigation. J. Mol. Catal. A, Chem. **307**(1–2), 43–50 (2009). doi:10.1016/j.molcata.2009.03.008

Ferreira, M.L., Volpe, M.: A combined theoretical and experimental study of supported vanadium oxide catalysts. J. Mol. Catal. A, Chem. **184**(1–2), 349–360 (2002)

Gerasimov, S.F., Filimonov, V.N.: Infrared-spectra of the photosorption products of hydrogen and carbon-monoxide on Al_2O_3 and SiO_2 containing transition-metal ions. Kinet. Catal. **22**(2), 359–362 (1981)

Gerasimov, S.F., Filimonov, V.N.: Infrared-spectra of nitric-oxide adsorbed on photoreduced V/SiO2 catalyst. React. Kinet. Catal. Lett. **25**(3–4), 273–275 (1984). doi:10.1007/bf02064414

Hadjiivanov, K., Concepcion, P., Knozinger, H.: Analysis of oxidation states of vanadium in vanadia-titania catalysts by the IR spectra of adsorbed NO. Top. Catal. **11**(1–4), 123–130 (2000)

Hadjiivanov, K.I.: Identification of neutral and charged NxOy surface species by IR spectroscopy. Catal. Rev. Sci. Eng. **42**(1–2), 71–144 (2000)

Hadjiivanov, K.I., Vayssilov, G.N.: Characterization of oxide surfaces and zeolites by carbon monoxide as an IR probe molecule. Adv. Catal. **47**(47), 307–511 (2002)

Hess, C.: Direct correlation of the dispersion and structure in vanadium oxide supported on silica SBA-15. J. Catal. **248**(1), 120–123 (2007)

Hess, C.: Nanostructured vanadium oxide model catalysts for selective oxidation reactions. ChemPhysChem **10**(2), 319–326 (2009). doi:10.1002/cphc.200800585

Ivanova, E., Hadjiivanov, K., Dzwigaj, S., Che, M.: FT-IR study of CO and NO adsorption on a VSiBEA zeolite. Microporous Mesoporous Mater. **89**(1–3), 69–77 (2006)

Jonson, B., Rebenstorf, B., Larsson, R.: An infrared spectroscopic investigation on co adsorbed on silica-supported vanadocene. Acta Chem. Scand., Ser. A, Phys. & Inorg. Chem. **42**(3), 156–164 (1988a). doi:10.3891/acta.chem.scand.42a-0156

Jonson, B., Rebenstorf, B., Larsson, R., Andersson, S.L.T.: Activity measurements and spectroscopic studies of the catalytic-oxidation of toluene over silica-supported vanadium-oxides. J. Chem. Soc. Faraday Trans. I **84**, 1897 (1988b). doi:10.1039/f19888401897

Kantcheva, M.M., Hadjiivanov, K.I., Klissurski, D.G.: An IR spectroscopy study of the state and localization of vanadium oxo species adsorbed on TiO2 (Anatase). J. Catal. **134**(1), 299–310 (1992)

Keller, D.E., Koningsberger, D.C., Weckhuysen, B.M.: Molecular structure of a supported VO4 cluster and its interfacial geometry as a function of the SiO2, Nb2O5, and ZrO2 support. J. Phys. Chem. B **110**(29), 14313–14325 (2006). doi:10.1021/jp060749h

Kung, H.H.: Oxidative dehydrogenation of light (C-2 to C-4) alkanes. In: Advances in Catalysis. Advances in Catalysis, vol. 40, pp. 1–38. Academic Press, San Diego (1994)

Liu, Y.M., Cao, Y., Yi, N., Feng, W.L., Dai, W.L., Yan, S.R., He, H.Y., Fan, K.N.: Vanadium oxide supported on mesoporous SBA-15 as highly selective catalysts in the oxidative dehydrogenation of propane. J. Catal. **224**(2), 417–428 (2004)

Martra, G., Arena, F., Coluccia, S., Frusteri, F., Parmaliana, A.: Factors controlling the selectivity of V2O5 supported catalysts in the oxidative dehydrogenation of propane. Catal. Today **63**(2–4), 197–207 (2000)

Nguyen, L.D., Loridant, S., Launay, H., Pigamo, A., Dubois, J.L., Millet, J.M.M.: Study of new catalysts based on vanadium oxide supported on mesoporous silica for the partial oxidation of methane to formaldehyde: catalytic properties and reaction mechanism. J. Catal. **237**(1), 38–48 (2006). doi:10.1016/j.jcat.2005.10.016

Setnicka, M., Bulanek, R., Capek, L., Cicmanec, P.: n-Butane oxidative dehydrogenation over VOX-HMS catalyst. J. Mol. Catal. A, Chem. **344**(1–2), 1–10 (2011). doi:10.1016/j.molcata.2011.05.004

Shenderovich, I.G., Buntkowsky, G., Schreiber, A., Gedat, E., Sharif, S., Albrecht, J., Golubev, N.S., Findenegg, G.H., Limbach, H.H.: Pyridine-n-15 - a mobile NMR sensor for surface acidity and surface defects of mesoporous silica. J. Phys. Chem. B **107**(43), 11924–11939 (2003). doi:10.1021/jp0349740

Schramlmarth, M., Wokaun, A., Pohl, M., Krauss, H.L.: Spectroscopic investigation of the structure of silica-supported vanadium-oxide catalysts at submonolayer coverages. J. Chem. Soc. Faraday Trans. **87**(16), 2635–2646 (1991). doi:10.1039/ft9918702635

Tian, H.J., Ross, E.I., Wachs, I.E.: Quantitative determination of the speciation of surface vanadium oxides and their catalytic activity. J. Phys. Chem. B **110**(19), 9593–9600 (2006). doi:10.1021/jp055767y

Tielens, F., Calatayud, M., Dzwigaj, S., Che, M.: What do vanadium framework sites look like in redox model silicate zeolites? Microporous Mesoporous Mater. **119**(1–3), 137–143 (2009)

Topsoe, N.Y., Topsoe, H., Dumesic, J.A.: Vanadia-titania catalysts for selective catalytic reduction (SCR) of nitric-oxide by ammonia .1. Combined temperature-programmed in-situ FTIR and online mass-spectroscopy studies. J. Catal. **151**(1), 226–240 (1995). doi:10.1006/jcat.1995.1024

VanDerVoort, P., White, M.G., Mitchell, M.B., Verberckmoes, A.A., Vansant, E.F.: The effect of water on the structure of supported vanadium oxide structures. An FT-RAMAN, in situ DRIFT and in situ UV-VIS diffuse reflectance study. Spectrochim. Acta, Part A, Mol. Biomol. Spectrosc. **53**(12), 2181–2187 (1997). doi:10.1016/s1386-1425(97)00145-5

Venkov, T.V., Hess, C., Jentoft, F.C.: Redox properties of vanadium ions in SBA-15-supported vanadium oxide: an FTIR spectroscopic study. Langmuir **23**(4), 1768–1777 (2007)

Zarubin, D.P.: The two-component bands at about 4500 and 800 cm-(1) in infrared spectra of hydroxyl-containing silicas. interpretation in terms of Fermi resonance. J. Non-Cryst. Solids **286**(1–2), 80–88 (2001). doi:10.1016/s0022-3093(01)00487-2

Zukal, A., Siklova, H., Cejka, J.: Grafting of alumina on SBA-15: effect of surface roughness. Langmuir **24**(17), 9837–9842 (2008)