A comparative study of V species in ß zeolite by photoluminescence, diffuse reflectance UV-Visible and ^{51}V NMR spectroscopies

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In calcined and rehydrated VSiß zeolite prepared following a method described earlier, three kinds of tetrahedral V^V species can be clearly identified by photoluminescence spectroscopy even at low V content, in contrast to ^{51}V NMR and diffuse reflectance UV-Visible spectroscopies which do not allow them to be distinguished. A comparative study by photoluminescence and ^{51}V NMR spectroscopies leads to the suggestion that there is a correlation between the vibrational energy of the V=O bond and the corresponding chemical shift of the ^{51}V NMR signal.

KEY WORDS: beta zeolite; tetrahedral vanadium species; vibrational fine structure; photoluminescence; diffuse reflectance UV-Visible; ^{51}V NMR

1. Introduction

Spectroscopic techniques, particularly UV-Visible, ESR, Raman, NMR and IR, are often applied to characterize V species in various materials [1–9]. Recently, we have shown [2] that catalytically active vanadium ions are dispersed in a dealuminated ß zeolite by contacting this material with aqueous ammonium metavanadate solution. From our IR, UV-Visible and ^{51}V NMR studies, the most common view is that these vanadium ions are present as tetrahedral V^V species [2,3]. However, despite the combined deployment of those techniques, it is difficult to conclude if in V-loaded ß zeolite there is a unique kind or a mixture of differents kinds of tetrahedral V^V species. Recently [4], we reported that three kinds of tetrahedral V^V species can be distinguished in VSiß zeolite with 1.5 wt% of V by photoluminescence spectroscopy and that their relative concentrations strongly depend on dehydration/rehydration treatments.

In this paper, a comparative study of V species by photoluminescence, diffuse reflectance UV-Visible and ^{51}V NMR spectroscopies is presented. It shows that photoluminescence spectroscopy can clearly identify three kinds of tetrahedral V^V species in calcined and rehydrated VSiß zeolite, particularly for a *very low V content (0.05 wt% of V)*, in contrast to ^{51}V NMR and diffuse reflectance UV-Visible spectroscopies which do not allow one to distinguish them. Moreover, this study allows us to suggest that there is a correlation between the vibrational energy of the V=O bond determined by photoluminescence and the corresponding chemical shift of the ^{51}V NMR signal.

2. Experimental

$V_{0.05}$Siß and $V_{1.5}$Siß (with 0.05 and 1.5 wt% of V, respectively) were prepared by a post-synthesis method described earlier [2]. After calcination at 773 K for 2 h and cooling to room temperature both performed in flowing dry oxygen (120 ml min^{-1}), the samples were rehydrated at 298 K in moist air for 30 h and labeled C-Hyd-$V_{0.05}$Siß and C-Hyd-$V_{1.5}$Siß, respectively, where C stands for calcined and Hyd for rehydrated. The colour of C-Hyd-$V_{0.05}$Siß is white and that of C-Hyd-$V_{1.5}$Siß yellow.

Photoluminescence measurements were carried out at 77 K with a Spex Fluorolog II spectrofluorimeter. The spectra were obtained under irradiation at 250 or 340 nm using an emission band pass of 0.5 nm, in order to better distinguish the different vibrational fine structures.

Diffuse reflectance UV-Visible spectra were registered at 298 K on a Cary 5E spectrometer with the parent V-free material as reference.

^{51}V wide-line and MAS NMR spectra were collected on a Bruker MSL 400 spectrometer working at 78.9 MHz (7.05 T). Wide-line spectra were recorded using a 500 kHz spectral window, a pulse length of 1.6 μs and a pulse delay of 2 s. MAS spectra were obtained using a single pulse sequence with a pulse length of 1 μs, a pulse delay of 0.5 s and a rotor spinning rate of 14 kHz. All chemical shifts were measured by reference to liquid $VOCl_3$ ($\delta = 0$ ppm), a spin-

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ning solid vanadia sample being used as a secondary reference for MAS experiments ($\delta = -609$ ppm).

3. Results and discussion

The ^{51}V wide-line NMR spectra of C-Hyd-V$_{0.05}$Siß and C-Hyd-V$_{0.05}$Siß are shown in figure 1. As established by simulation, in the ^{51}V wide-line NMR spectrum of C-Hyd-V$_{0.05}$Siß a single orthorhombic signal with a maximum at -535 ppm is detected. A similar signal has been already reported for calcined V–Ti silicalites, V–Al silicalites and KVS-5 and assigned to V^{V} in a tetrahedral environment [5]. In contrast, the ^{51}V wide-line NMR spectrum of C-Hyd-V$_{1.5}$Siß is composed of an orthorhombic signal with a maximum at -605 ppm and of a band with a maximum at -350 ppm. The former is likely to be due to V^{V} in a distorted VO$_4$ tetrahedral environment and the latter, quite different from that of V$_2$O$_5$, to V^{V} in an axially distorted octahedral environment, on the basis of results obtained with reference solid compounds [6].

It is known ([9], and references herein) that ^{51}V MAS NMR can bring additional information on V species. Probably due to the very small amount of V, no ^{51}V MAS NMR signal is observed for C-Hyd-V$_{0.05}$Siß. In contrast, for C-Hyd-V$_{1.5}$Siß signals of tetrahedral and octahedral V are visible with an isotropic chemical shift $\delta_{\rm iso}$(MAS) of -698 and -559 ppm, respectively (figure 2). Similar signals have been reported for the V$_2$O$_5$/SiO$_2$ system [10].

The diffuse reflectance UV-Visible spectrum of C-Hyd-V$_{0.05}$Siß exhibits two bands at 270 and 340 nm (figure 3), very similar to those observed for as-prepared V$_{0.05}$Siß. Due to the absence of (d–d) transition in the range 600–800 nm and of any V^{IV} ESR signal, these bands can only involve V^{V} ions. They are attributed to $\pi(t_2) \rightarrow$ d(e) and to $\pi(t_1) \rightarrow$ d(e) oxygen-to-tetrahedral V^{V} charge transfer transitions, involving oxygen in bridging (V–O–Si) and terminal (V=O) positions, respectively, in agreement with earlier results [7,8]. The UV-Visible spectrum indicates the presence in C-Hyd-V$_{0.05}$Siß of only one kind of tetrahedral V^{V}, in agreement with the ^{51}V wide-line NMR results.

In contrast, the UV-Visible spectrum of C-Hyd-V$_{1.5}$Siß is composed of two intense charge transfer bands at 375 and 265 nm with a shoulder at 235 nm. As reported earlier [7], the band at 375 nm can be attributed to an oxygen-to-octahedral V^{V} charge transfer transition with oxygen in terminal position (V=O) and the bands at around 235–270 nm

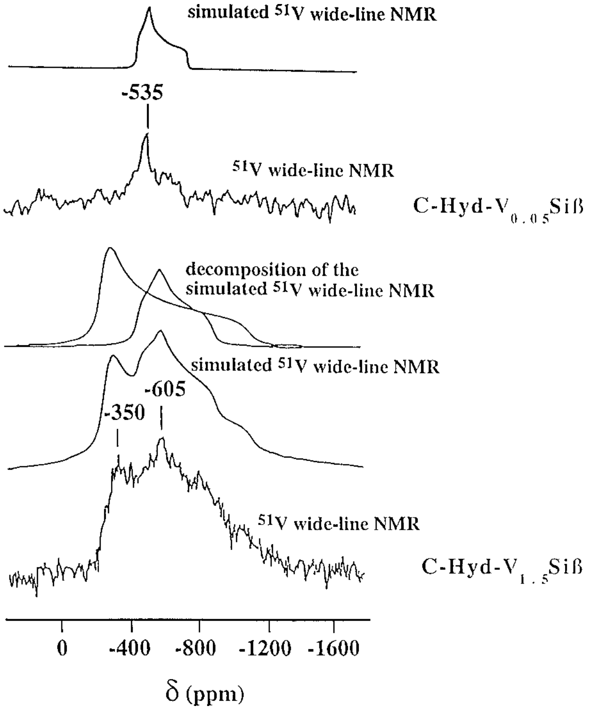

Figure 1. 78.9 MHz ^{51}V wide-line NMR and simulated spectra of C-Hyd-V$_{1.5}$Siß and C-Hyd-V$_{0.05}$Siß.

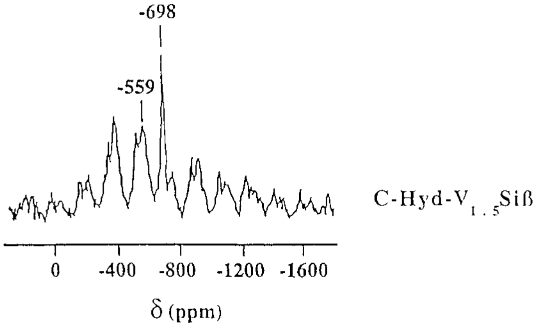

Figure 2. ^{51}V MAS NMR spectrum of C-Hyd-V$_{1.5}$Siß. Any signal was observed for C-Hyd-V$_{0.05}$Siß.

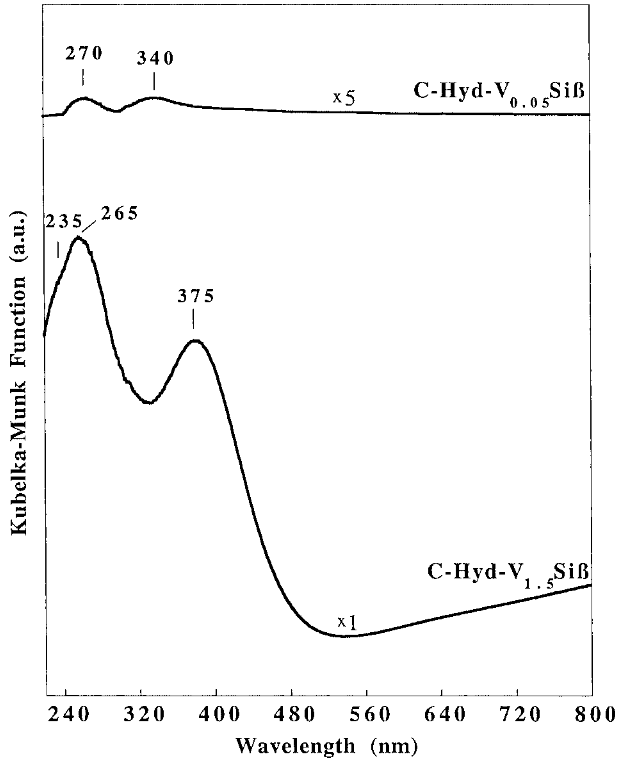

Figure 3. Diffuse reflectance UV-Visible spectra of C-Hyd-V$_{1.5}$Siß and C-Hyd-V$_{0.05}$Siß, measured at 298 K, using the parent V-free Siß zeolite as reference.

to $\pi(t_2) \rightarrow$ d(e) oxygen-to-tetrahedral V^V charge transfer transition with oxygen in bridging position (V–O–Si). The shoulder at 235 and the band at 265 nm suggest the presence of two different kinds of tetrahedral V^V, strongly and less distorted, respectively, in agreement with the results reported for $KVOF_4$ and the VO_4^{3-} complex [11,12]. The major part of V species is present in less distorted tetrahedral (band at 265 nm) and in octahedral V species (band at 375 nm). The presence of tetrahedral V^V species in calcined and rehydrated C-Hyd-$V_{1.5}$Siß suggests that some of V^V centres are not accessible to water molecules and retain their tetrahedral coordination even in the rehydrated form of the zeolite.

The C-Hyd-$V_{1.5}$Siß and C-Hyd-$V_{0.05}$Siß samples exhibit photoluminescence spectra with maxima at around 500 nm together with complex vibrational fine structures (figure 4). These spectra correspond to transitions from the lowest vibrational level of the excited triplet state $T_1(V^{4+}–O^-)$ to the various vibrational levels of the ground singlet state $S_0(V^{5+}=O^{2-})$, as described earlier [4,13]. The fact that the same spectra are obtained under irradiation at 250 or 340 nm suggests that the electronic state from which the emission process occurs is identical and independent of the absorption energy in the range 250–340 nm.

In order to ease the analysis of the very complex spectra due to the superimposition of different vibrational fine structures, the second-derivative presentation was used (figure 5). We wish to underline that even with the sample with the lower V content, three different types of vibrational fine structure can be clearly distinguished which can be related to three (α, β, γ) different kinds of tetrahedral V^V species.

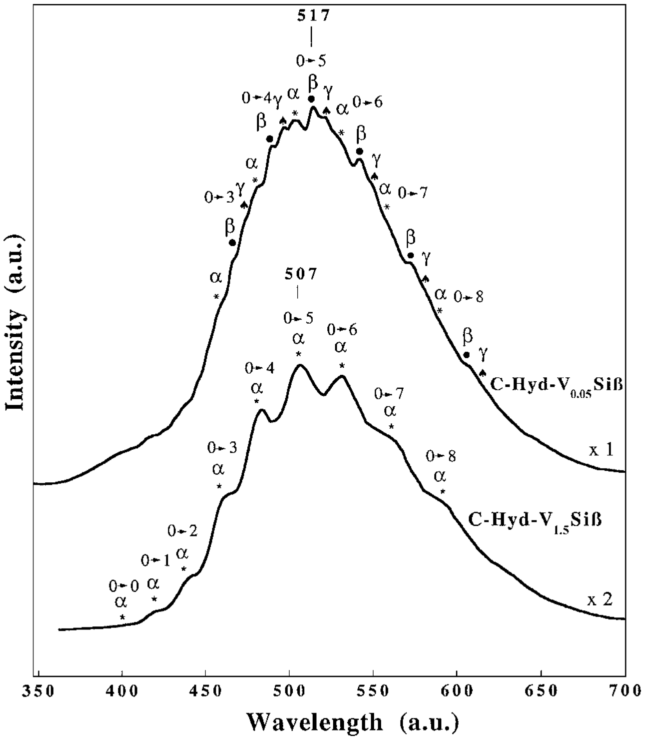

Figure 4. Photoluminescence spectra at 77 K of C-Hyd-$V_{1.5}$Siß and C-Hyd-$V_{0.05}$Siß outgassed at 473 K for 2 h (10^{-3} Pa).

For C-Hyd-$V_{1.5}$Siß, the spectrum is less resolved than for C-Hyd-$V_{0.05}$Siß and exhibits mainly the α type species. This latter has a shorter lifetime (28 ms) of the excited triplet state as compared to the other two species (β 88 ms, γ 49 ms), which indicates that the thermal deactivation process is dominant and the photoluminescence yield is lower for the α type species. Because the C-Hyd-$V_{1.5}$Siß sample leads mainly to α species, the intensity of its photoluminescence spectrum is significantly decreased as compared to C-Hyd-$V_{0.05}$Siß.

The second-derivative photoluminescence spectra of the above samples are not strongly affected by the presence of silanol groups and the energy separation between the $(0 \rightarrow 0)$ and $(0 \rightarrow 1)$ vibrational transitions can thus be determined for each V species. The vibrational energy calculated from the second derivative spectrum of the α species corresponds with 1018 cm^{-1}, that of β with 1054 cm^{-1} and that of γ with 1036 cm^{-1} in good agreement with the vibrational energy of the surface V=O bond obtained by IR [13,14] and Raman [15,16] measurements for gaseous (VOF_3) and liquid ($VOCl_3$ and $VOBr_3$) molecular compounds [17,18] and various oxide-supported vanadium solid catalysts (V_2O_5/SiO_2 and V_2O_5/PVG [13,15], and $V_2O_5/\gamma\text{-}Al_2O_3$ [16]).

On the basis of the linear correlation between the wavenumber of the V=O bond and its length in several V compounds [14], bond lengths of 1.54, 1.56, and 1.58 Å are obtained for the V=O of β, γ and α, respectively. Upon increase of the V=O bond length, the symmetry of V species moves toward the pure tetrahedral one.

The chemical shift of the orthorhombic ^{51}V wide-line NMR signal more important for C-Hyd-$V_{1.5}$Siß (−605 ppm) than for C-Hyd-$V_{0.05}$Siß (−535 ppm) can be related to the higher symmetry of the tetrahedral V^V species in the former

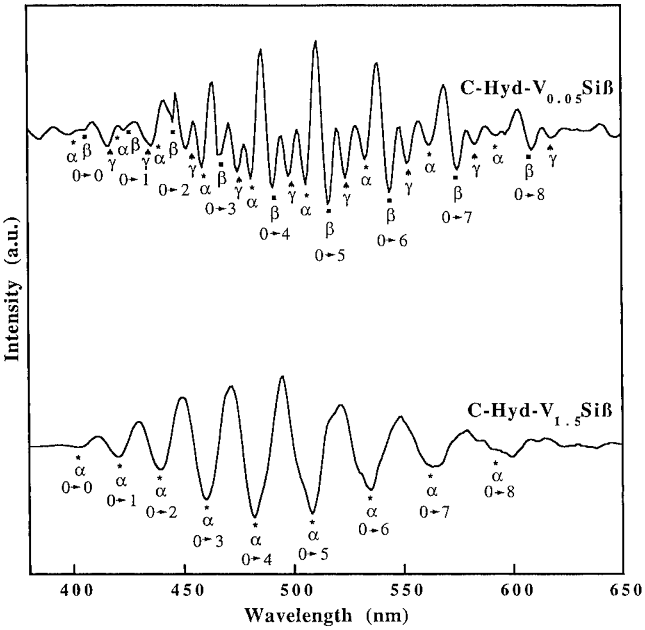

Figure 5. Second derivative of the photoluminescence spectra at 77 K of C-Hyd-$V_{1.5}$Siß and C-Hyd-$V_{0.05}$Siß outgassed at 473 K for 2 h (10^{-3} Pa).

sample, in agreement with the results reported for a series of vanadates [6].

The comparative study of V species by photoluminescence and ^{51}V NMR spectroscopies allows us to suggest that there is a correlation between the vibrational energy of the V=O bond and the corresponding chemical shift of the ^{51}V NMR signal. Indeed, we observe that the vibrational energy decreases in the following order: $\beta > \gamma > \alpha$, while the chemical shift increases from -535 ppm for the mixture of α, β, γ species to -605 ppm for the α one. For VO_4^{3-} species with nearly ideal tetrahedral V^V symmetry, the chemical shift is found to be at approximately -740 ppm [19]. These results on tetrahedral V^V species suggest that, when the symmetry increases, the vibrational energy decreases while the chemical shift increases.

Moreover, in sample C-Hyd-$V_{0.05}$Siß with the low V content, coordination of water to the tetrahedral V^V sites does not occur since it does not lead to octahedral V^V suggesting that V^V ions are in poorly accessible sites, such as S1 sites in the 5-membered rings of the ß structure [20]. In contrast, for higher V content, V^V ions are in more accessible sites, such as S2 sites in the 12-membered rings, where they can easily change their coordination upon calcination/rehydration treatments, as shown earlier [20].

4. Conclusions

In conclusion, the present results show that photoluminescence spectroscopy, while not detecting octahedral V^V species [13], is far more sensitive than UV-Visible and ^{51}V NMR spectroscopies to detect and discriminate different kinds of tetrahedral V species in C-Hyd-VSiß zeolite, particularly at low V content. The three kinds of tetrahedral V^V species distinguished by photoluminescence spectroscopy are present in two different framework sites, such as S1 and S2 sites in 5- and 12-membered rings, respectively, of the ß zeolite.

The presence of different kinds of tetrahedral V^V species in V-loaded zeolite may have important impact on its catalytic activity. As already observed [21], the environment of vanadium is a key parameter which controls the mild oxidation of light alkanes. The catalytic activity of VSiß zeolite is presently examined in the reaction of oxidative dehydrogenation of alkane.

Moreover, the comparative study by photoluminescence and ^{51}V NMR leads us to suggest that there is a correlation between the vibrational energy of the V=O bond and the corresponding chemical shift of the ^{51}V NMR signal.

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