Probing Different Kinds of Vanadium Species in the VSi*β* Zeolite by Diffuse Reflectance UV−Visible and Photoluminescence Spectroscopies

Stanislaw Dzwigaj,*,† Masaya Matsuoka,*,† Raymonde Franck,*,‡ Masakazu Anpo,§ and Michel Che†,‖

Laboratoire de Réactivité de Surface, UNR 7609-CNRS, Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France, Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Sakai, Osaka 599-8531, Japan, and Institut Universitaire de France

The presence of different vanadium species in VSi*β* zeolite is evidenced by diffuse reflectance UV−visible and photoluminescence spectroscopies, but only the latter is able to clearly distinguish three kinds of tetracoordinated vanadium sites and to reveal the effects of V loading and dehydration−hydration processes on the environment of the V species.

Introduction

In recent years, increasing attention has been directed toward the study of new zeolitic materials, especially crystalline microporous metallosilicates that possess interesting catalytic properties.[1−4] In particular, attention has been focused on vanadium-containing silicate molecular sieves.[4−7] These materials with highly dispersed vanadium can be prepared not only by hydrothermal synthesis[5,7] but also by postsynthesis methods.[4,8−11] The deposition of vanadium on acid catalysts, leading to their gradual poisoning, and its removal for regeneration are also very important problems in fluid catalytic cracking (FCC) processes.[12,13] In a previous paper,[11] we have shown that an aqueous solution of ammonium metavanadate can be used to incorporate vanadium in a dealuminated Si*β* zeolite as isolated tetracoordinated V species. In the VSi*β* sample the broad UV−visible bands at 270 and 340 nm together with the two framework IR bands at 950 and 980 cm^{-1}, indicative of the stretching mode of a SiO$_4$ unit bonded to a metal ion,[11] suggested that there was a mixture of different tetracoordinated V species.

Since it is now widely accepted that the active sites of selective oxidation of alkenes are isolated, tetracoordinated transition metal cations,[1,14] we have tried to clarify the vanadium environment in the VSi*β* zeolite by means of diffuse reflectance UV−visible and photoluminescence spectroscopies. In the present study, these two techniques used in combination reveal the presence of three kinds of tetracoordinated vanadium sites in the VSi*β* zeolite; their relative amounts depend strongly on the V loading and on dehydration−hydration processes.

Experimental Section

The VSi*β* sample was prepared by introducing 2.3 g of a Si*β* zeolite (Si/Al > 1300), dealuminated by treatment of TEA*β* (Si/Al = 11) in a 13 M HNO$_3$ solution for 4 h at 353 K,[11] in 10 mL of an aqueous solution of ammonium metavanadate (7 10^{-2} mol·L^{-1}) at 298 K for 3 days without any stirring.[11] The solid recovered by centrifugation and dried at 353 K overnight contained 1.5 wt % of V and was labeled VSi*β*. It was further calcined at 773 K for 2 h in flowing oxygen and denoted C-VSi*β*. This sample was then hydrated at 298 K in moist air and labeled C-Hyd-VSi*β*, where C stands for calcined and Hyd for hydrated.

The diffuse reflectance UV−visible spectra were recorded at 298 K on a Cary spectrometer, and photoluminescence measurements were carried out at 77 K with a Spex Fluorolog II spectrofluorimeter using a quartz cell equipped with a stopcock allowing further adsorption and thermal treatments to be performed.

Results and Discussion

The higher values of the asymmetric stretching of the T−O bond (ν_{as}) (IR spectra) and of the d_{302} spacing (XRD diffractograms) for VSi*β* relative to those for the parent Si*β* sample[11] suggest that vanadium ions are incorporated into the zeolite *β* framework[15,16] and thus tetracoordinated. Since UV−visible spectroscopy is a well-accepted technique for confirmation of isomorphous incorporation of metal ions at lattice positions in the zeolites and related materials,[5,7,8,17] it was used to study the nature of V species in VSi*β* zeolite. The absence of (d−d) transitions in the diffuse reflectance UV−visible spectra of the VSi*β*, C-VSi*β*, and C-Hyd-VSi*β* samples (Figure 1) in the range 600−800 nm and the presence of only very weak signals of V^{IV} registered (not shown) by the more sensitive EPR technique clearly indicate that the amount of reduced V^{IV} species in these samples is negligible. For the VSi*β* sample, two broad bands at 270 and 340 nm are observed in the UV−visible spectrum, which can be assigned to ligand-to-metal charge-transfer transitions, in the present case from the oxygen ligands to a tetracoordinated vanadium V^V ion.[5,9,11,18] The UV−visible spectrum of the C-VSi*β* sample is composed of a broad band in the 230−340 nm range, with a maximum at 235 nm and a shoulder at 265 nm (Figure 1b). The shift of the charge-transfer bands to an energy higher than that observed for the VSi*β* sample, coupled with the simultaneous decrease in their intensities, suggests[19,20] a greater distortion of the tetracoordinated V^V species in the C-VSi*β* sample. Upon exposure of C-VSi*β* to

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* To whom correspondence should be addressed. Phone, 33-(1)-44275515; fax, 33-(1)-44276033; e-mail, dzwigaj@ccr.jussieu.fr.
† Université P. et M. Curie.
‡ Deceased.
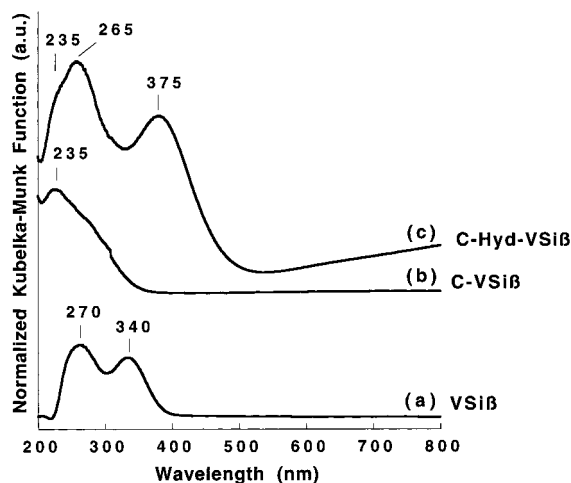§ Osaka Prefecture University.
‖ Institut Universitaire de France.

Figure 1. Diffuse reflectance UV−Visible spectra of VSiβ (a), of C-VSiβ (b), and of C-Hyd-VSiβ (c), measured using the parent V-free Siβ zeolites as reference.
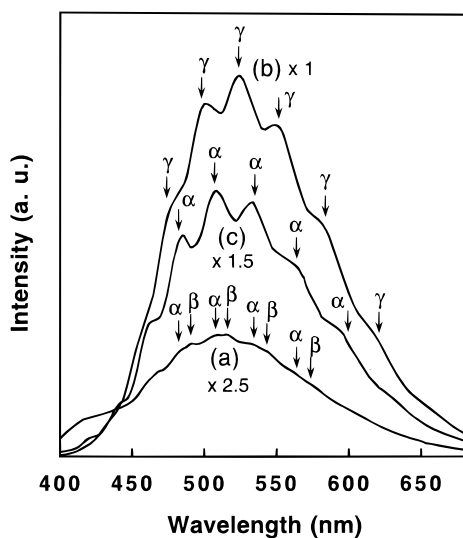

Figure 2. Photoluminescence spectra of VSiβ evacuated at 353 K for 2 h (10^{-5} Torr) (a), of C-VSiβ evacuated at 473 K for 2 h (10^{-5} Torr) (b), and of C-Hyd-VSiβ evacuated at 473 K for 2 h (10^{-5} Torr) (c).

Figure 3. Second derivative of the photoluminescence spectra of VSiβ evacuated at 353 K for 2 h (10^{-5} Torr) (a), of C-VSiβ evacuated at 473 K for 2 h (10^{-5} Torr) (b), and of C−Hyd-VSiβ evacuated at 473 K for 2 h (10^{-5} Torr) (c). The decay curves (insets a, b, and c, logarithmic scale) were monitored at 77 K with a Spex 1934D phosphorimeter at the emission of 520 nm. Lifetimes were calculated from the average slope between 2 and 60 ms.

moist air, the color of the sample changes rapidly from white to yellow, and two intense bands at 265 and 375 nm with a shoulder at 235 nm appear in the UV−visible spectrum (Figure 1c). This suggests that some of the more distorted tetracoordinated V species (band at 235 nm) are still present in the C-Hyd-VSiβ sample but the major part of this species is transformed to less distorted tetracoordinated V species (band at 265 nm) and to square pyramidal or octahedral V species (band at 375 nm).[21] Upon calcination of C-Hyd-VSiβ at 773 K for 2 h in flowing oxygen, the initial spectrum of the C-VSiβ sample is restored (Figure 1b). The subsequent exposure of the latter sample to moist air resulted in a UV−visible spectrum similar to that observed for C-Hyd-VSiβ sample (Figure 1c), indicating that the dehydration (during calcination) and hydration (upon exposure to moist air) processes are reversible.

To clarify the nature of the vanadium species, the photoluminescence spectra of the VSiβ, C-VSiβ, and C−Hyd-VSiβ samples (excitation wavelength, 250 nm) have been recorded (Figure 2). These samples exhibit photoluminescence spectra with maxima at around 500 nm together with a vibrational fine structure. This fine structure corresponds to transitions from the lowest vibrational level of the excited triplet state T_1($V^{4+}-$
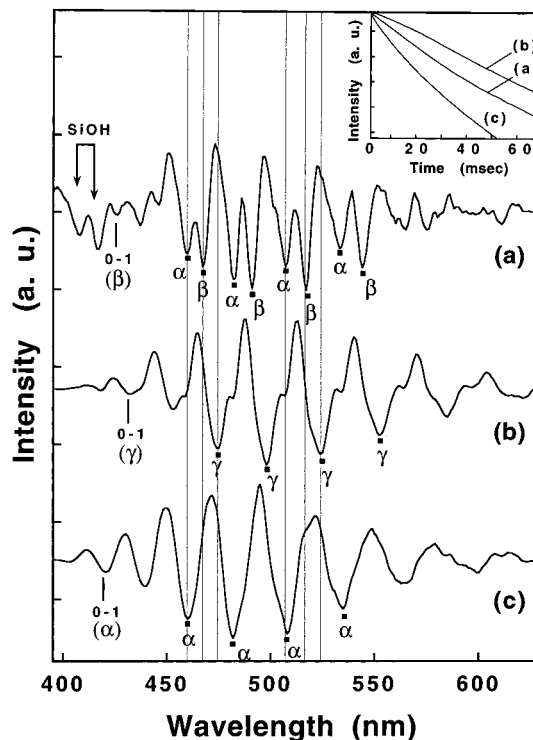
O^-) to the various vibrational levels of the ground singlet state S_0($V^{5+}=O^{2-}$).[9,22−27] The shapes and positions of the maxima as well as the intensities of the components of the fine structure strongly depend on the pretreatment of the samples. Three vibrational fine structures can be distinguished in the photoluminescence spectra of the VSiβ samples (Figure 2), related to the presence of three different kinds of tetracoordinated V species (α, β, γ).

For the VSiβ sample, the separation of the vibrational bands is not very well resolved owing to the superposition of different sets of vibrational fine structure involving tetracoordinated V species of different symmetries. In fact, the second derivative phosphorescence spectrum (Figure 3a) of this sample clearly shows the presence of two (α and β) main tetracoordinated V species, the intensity of the third one (γ) being very weak. It is possible to clearly determine the energy of the $0 \rightarrow 1$ transition since in this region the spectrum is not strongly affected by the silanol groups (Figure 3). The vibrational energy calculated from the second-derivative spectrum of the V species (β) corresponds to 1054 cm^{-1} indicating a very short V=O bond length (1.54 Å). The bond length has been calculated on the basis of the correlation between the wavenumber of the V=O bond and its bond length.[26]

As seen in Figure 2b, the vibrational bands are more intense and better resolved for the C-VSiβ than for the VSiβ sample and their maximum is shifted to higher wavelength. The second-derivative phosphorescence spectrum (Figure 3b) clearly shows that, in this sample, three tetracoordinated V species are also present; the γ type is, however, the most important one. The vibrational energy of the γ type V species corresponds to 1036 cm^{-1}, which indicates a longer V=O bond length (1.56 Å) and higher symmetry (with an increase in the length of the

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TABLE 1

type of tetracoordinated V species	α	γ	β
vibrational energy (cm^{-1})	1018	1036	1054
V=O bond length (Å)	1.58	1.56	1.54
V−O single bonds lengths (Å) 1.72−1.80^a			
O=V−O(Si,H) bond angle (labeled θ, Scheme 1)	θ_α <	θ_γ <	θ_β
lifetime of the excited triplet states (ms)	28	49	88

^{a} Data for reference compounds containing isolated VO$_4$ tetrahedra taken from ref 31.

SCHEME 1

X = O-(Si,H)
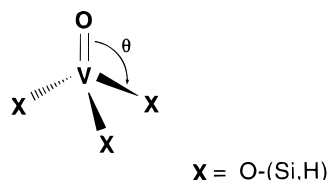
double bond toward that of the corresponding single bond with the symmetry of the tetracoordinated V species moving closer to the ideal T_d symmetry) of this species in comparison with those of the β species.

The vibrational bands are less intense for C-Hyd-VSiβ sample (Figure 2c), and their maximum is shifted to lower wavelengths by comparison with the C-VSiβ sample. The second-derivative spectrum (Figure 3c) shows that for the C-Hyd-VSiβ sample the α type tetracoordinated V species is the main species, and its formation, in this case, is probably related to the hydrolysis of the V−O−Si bridge[28] of the strongly distorted γ species. The vibrational energy of the α species corresponds to 1018 cm^{-1}, which indicates a longer V=O bond length (1.58 Å) and higher symmetry of the α than of the γ species. The vibrational energy found for the α, β, and γ tetracoordinated V species is in good agreement with the energy of the vibration of the double bond in surface vanadyl groups.[23] Both the V=O bond length and the symmetry of the V species decrease in the following order: α > γ > β, while the O=V−O(Si,H) bond angle increases, on the basis of VSEPR arguments.[29]

The lifetimes of the excited triplet states have been determined from the decay curves of the photoluminescence of VSiβ (inset a), C-VSiβ (inset b) and C-Hyd-VSiβ (inset c), respectively (Figure 3). They were found to be 40 ms for the mixture of the α and β type V species, 49 ms for the γ type and 28 ms for the α type. Moreover, we have observed that with a much lower V loading (0.05 wt %) than for the VSiβ sample, the main species is β in the calcined sample, and its lifetime (88 ms) is longer than that for the C-VSiβ sample.[30] Since the decay time of the triplet-to-singlet emission increases with degree of distortion of tetrahedral coordination of metal ions (V^{5+}, Ti^{4+}, Nb^{5+}) from the ideal T_d[18], the increase in the lifetime from 28 to 88 ms for the sequence of the α → γ → β species can be interpreted in terms of the increase in the distortion of the tetracoordinated V species and the decrease of the V=O bond length. We are thus able to propose that the three tetracoordinated V species are due to three different framework sites, which have different O=V−O(Si,H) bond angles and V=O bond lengths (Table 1 and Scheme 1).

Moreover, the long lifetimes of the excited triplet states of the β (88 ms) and γ (49 ms) type V species, much longer than those obtained with impregnated vanadium oxides[32] or with anchored vanadium oxide prepared by the photo-CVD method,[9] suggest that vanadium ions within the VSiβ zeolite are highly

dispersed. As shown in the UV−visible spectra (Figure 1c), hydration of the C-VSiβ sample not only induces changes in the symmetry of the tetracoordinated V species but also leads to the formation of octahedral V species.

Conclusion

The presence of different types of V species in VSiβ zeolite can be detected by diffuse reflectance UV−visible and photoluminescence spectroscopies, but only the latter is able to clearly distinguish three different kinds of signals (α, β, and γ) each corresponding to tetracoordinated V ions. From static and dynamic photoluminescence measurements, more precise information has been obtained on the different types of V species, in terms of vibrational energy, V=O bond length, O=V−O(Si,H) bond angle, and lifetime of the excited triplet states. These results show that photoluminescence spectroscopy can provide very precise information on the symmetry of V sites, which is very difficult to obtain with other techniques such as UV−visible or NMR. Further studies are underway to complement the description of the V sites, particularly by adsorption of probe molecules and EXAFS. In addition, the photocatalytic and catalytic activities of these materials will be examined. To the best of our knowledge, this is the first time that three different kinds of tetracoordinated V species have been identified within a zeolite structure.

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