

Role of silanol groups in the incorporation of V in β zeolite

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Received 28 January 1999; accepted 16 June 1999

Abstract

Aqueous solutions of ammonium metavanadate of increasing concentrations have been contacted with a β zeolite before (sample Al β , Si/Al = 11) and after (sample Si β , Si/Al > 1000) dealumination in a 13 N HNO₃ solution. UV–visible and ⁵¹V NMR characterizations of the V-loaded zeolites show that mainly octahedral V species are formed in Al β whereas, up to a loading of 1.75 V atoms per unit cell (2.3 V wt.%), only pseudotetrahedral V species (nonhydroxylated (SiO)₃V=O and hydroxylated (SiO)₂(HO)V=O) are observed in Si β . XRD and FT-IR results indicate that the V atoms present in Si β are incorporated in the framework in a pseudotetrahedral environment. These V species are resistant to washing either with water or with an aqueous solution of NH₄OAc (1 mol l⁻¹, 12 h). In contrast, the octahedral V species present in VAl β (whatever the V loading) and in VSi β (at loadings higher than 1.75 V per unit cell) are eliminated upon washing showing that these species are loosely bound to the zeolite. As demonstrated by FT-IR, the incorporation of V in the Si β framework involves silanol groups formed upon dealumination. This incorporation generates new Brönsted acidic sites. New FT-IR bands (3650, 3620, 980, 950 cm⁻¹) are formed whose attribution is proposed. The maximum amount of V atoms incorporated in Si β (1.75 per unit cell) is lower than the potential amount of framework vacant T-sites generated by dealuminating the β framework (5.3 per unit cell). However, this V amount is 20 times larger than that usually found in V-loaded zeolite prepared by hydrothermal synthesis. Therefore, this study confirms that dealuminating a zeolite is an attractive method to generate silanol groups which can be used to react with vanadium complexes and allow the incorporation in the zeolitic walls of high amounts of V atoms resistant to washing treatments. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Beta zeolite; Dealumination; Silanols; Vanadium; Incorporation

1. Introduction

V-loaded zeolites are active for oxidation reactions while still presenting shape selectivity of the parent zeolite. These solids selectively

catalyse side chain oxidations of alkylaromatics in the liquid phase, using H₂O₂ as an oxidant [1]. They are also able to oxidize various organics in the gas phase in the presence of oxygen (propane oxidative dehydrogenation [2], toluene oxidation to benzaldehyde and phenol [3]). A substantial amount of work has therefore been devoted to the preparation of V-loaded silicates (V-silicalite [4–6], VS-1 [7,8], VS-2 [9,10]) and aluminosilicates (V-ZSM-5 [6,12], V-ZSM-12

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[13,14], V-ZSM-22 [15], V-ZSM-48 [16], V- β [17,18]).

To obtain V-loaded zeolites, a vanadium precursor can be added during the hydrothermal synthesis of the zeolite [4–18]. Unlike the situation of titanium which is known to be directly incorporated in framework position by this method [19–21], the incorporation of vanadium is still considered as a challenge. It has been proposed that the incorporation of vanadium into the lattice occurs at defect sites [5,8,13]. However, most of the V species introduced during the synthesis remain loosely bound to the zeolite and they are eliminated during washing with ammonium acetate and/or when the V-loaded zeolites are used as catalysts in a liquid medium [5,6,8].

An alternative two-step method has been proposed by Kraushaar and Van Hooff [22]. In the first step, an aluminosilicate zeolite (ZSM-5) is dealuminated by a strong acidic treatment in order to form framework vacant T-sites associated with silanol groups. In the second step, the silanol groups thus generated are used as functional groups on which to attach transition metal species. Under highly demanding conditions such as a perfectly anhydrous atmosphere and at high temperature (typically in the range of 673–773 K), these silanol groups have been found to react with an easily hydrolyzed metallic precursor such as titanium tetrachloride [22,23].

For vanadium, the two-step method and the possibility of using less demanding conditions have been tested [24,25]. Firstly, Kim et al. [24] have tried to incorporate vanadium by an impregnation/calcination method in a previously dealuminated mordenite (Si/Al = 64). However, no V incorporation in the framework was observed and the bright orange color of the calcined V-loaded mordenite samples revealed the presence of polymeric vanadium species [9,10,17]. The formation of these polymeric species can most probably be explained by the strongly basic medium (pH of 13) maintained by addition of ammonia during the impregnation which is consistent with the well-known

aqueous chemistry of V species [26]. More recently [25], we have contacted for a few hours a previously dealuminated β zeolite with an aqueous solution of ammonium metavanadate (pH of the suspension of 2.5). After drying at 353 K in air, the V-loaded β samples were white and they were found to be active in oxidation reactions such as toluene hydroxylation. Moreover, preliminary UV–visible, ^{29}Si NMR and FT-IR characterizations suggested the presence in these samples of pseudotetrahedral V species, similar to the ones found for V-loaded silica-based supports (amorphous silica [28–30], mesoporous materials of the M41S family [27]). To understand further the nature of the bonding of these pseudotetrahedral V species to the β zeolite walls, we describe here a series of V-loaded β zeolites corresponding to increasing amount of vanadium, prepared by contacting a nondealuminated (Al β) and a dealuminated (Si β) β zeolites with aqueous NH_4VO_3 solutions of controlled concentrations. These samples are characterized by macroscopic (chemical analysis, BET, XRD) and microscopic (FT-IR, ^{51}V NMR, UV–visible) techniques before and after washing with water or with an aqueous NH_4OAc solution (1 mol l^{-1} , 12 h).

2. Experimental

2.1. Materials

The initial TEA- β zeolite (Si/Al ratio of 11, low Na content with Na/Al < 0.1) was provided in its tetraethylammonium templated form by RIPP-China. On one hand, this sample was calcined in air (823 K, 8 h, 100 K/h) to give the acidic Al-containing zeolite (sample Al β , Si/Al = 11). On the other hand, the TEA- β was dealuminated by concentrated nitric acid (HNO_3 , 13 N; 353 K; 4 h), according to a procedure already reported by Bourgeat-Lami et al. [31]. The dealuminated zeolite thus obtained (sample Si β) has an atomic Si/Al ratio greater than 1000.

Suspensions were prepared by pouring 2.3 g of either Al β or Si β in aqueous solutions of NH₄VO₃ (between 10 and 20 ml of solution, concentrations ranging from 1.25×10^{-2} to 7×10^{-2} mol l⁻¹). The desired amount of V species (V atoms per gram of zeolite) in the suspensions are summarized in Table 1. After 3 days of evolution at room temperature without stirring, V-loaded solids (labelled VAl β or VSi β) were recovered by centrifugation, dried at 353 K overnight and rehydrated in ambient conditions.

VSi β and VAl β samples were characterized before and after washing with distilled water (200 mg of zeolite in 20 ml of water, 7 h under stirring at room temperature) or with an aqueous solution of ammonium acetate (200 mg of solid in 20 ml of 1 mol l⁻¹ NH₄OAc, 12 h under stirring at room temperature) without any further calcination except for the IR experiments which were performed on self-supported wafers and required a preliminary dehydration step, as detailed thereafter.

2.2. Methods

Chemical analyses (Service Central d'Analyse, CNRS, Solaize, France) gave the molar Si/Al ratios and the numbers of V atoms per β

unit cell (64 TO₄ with T = Si, Al tetrahedral units) in the V-loaded zeolites. These numbers, reported in Table 1, are indicated when necessary as x and y indexes in V _{x} Si β and V _{y} Al β formulas.

Microporous volumes were estimated with an ASP 2010 apparatus (Micromeritics). All samples were outgassed initially at room temperature then at 623 K until a pressure < 0.2 Pa was achieved. The pore-size distributions were obtained by a single-point t -plot procedure [32]. Microporous volumes were calculated using Barrett, Joyner and Halenda (BJH) equations [32]. Powder X-ray diffractograms were recorded on a Siemens D5000 using the Cu K α radiation.

Transmission FT-IR spectra were recorded at room temperature on a Bruker IFS 66 V spectrometer, with a resolution of 2 cm⁻¹ either on KBr pellets or on self-supported wafers. Previous to measurements, the wafers were dehydrated under flowing oxygen (120 ml/min, 8 h) at 573 K (heating rate of 100 K/h) then evacuated for 6 h at the same temperature in a cell. Gaseous pyridine was directly contacted with the dehydrated wafers by opening a connection between the cell and an independent compartment containing liquid pyridine. Physisorbed pyridine was eliminated by evacuating the cell

Table 1

V content in the NH₄VO₃ suspensions, and in the V-loaded β zeolites before and after washing with H₂O or NH₄OAc and yield of V introduction in the solids

Starting zeolite	V content in the NH ₄ VO ₃ suspensions (10 ⁻⁴ V atoms/g zeolite)	V content (V atoms/ β unit cell) in the V-loaded β zeolites and (yield ^a of V introduction in the solid)		
		Before washing	After washing with H ₂ O	After washing with NH ₄ OAc
Al β	1.1	0.20 (44)	0.06 (10)	0.01 (3)
	3.2	0.64 (47)	0.06 (5)	0.01 (1)
Si β	–	–	–	–
	0.5	0.20 (100)	–	–
	1.1	0.45 (100)	0.45 (100)	0.45 (100)
	2.0	0.84 (100)	0.84 (100)	0.84 (100)
	3.2	1.35 (100)	–	–
	4.1	1.75 (100)	–	1.54 (90)
	5.3	1.86 (82)	1.61 (70)	1.61 (70)
7.6	2.00 (65)	1.66 (53)	1.61 (50)	

^aRatio of the number of V atoms in the solids divided by the initial number of V atoms introduced in the NH₄VO₃ suspensions.

at 423 K for 1 h. The photoacoustic IR spectra were recorded with a resolution of 4 cm^{-1} using an MTEC detector and He as a gas vector, on a Nicolet Magna 850 spectrometer.

^{51}V wide-line and MAS solid-state NMR spectra were collected on a Bruker MSM 400 spectrometer apparatus working at 78.9 MHz (7.05 T). Wide-line spectra were recorded using a 500-kHz spectral window, a pulse length of $1.6\ \mu\text{s}$ and a pulse delay of 2 s. The MAS spectra were obtained using a single-pulse sequence with a pulse length of $1\ \mu\text{s}$, a pulse delay of 0.5 s and a rotor spinning rate of 14 kHz. All chemical shifts were referred to liquid VOCl_3 ($\delta = 0\text{ ppm}$), a spinning solid vanadia sample being used as a secondary reference for MAS experiments ($\delta = -609\text{ ppm}$).

The diffuse reflectance UV–visible spectra of the V-loaded zeolites in their hydrated state were recorded on a Cary spectrometer equipped with a diffuse reflectance attachment, after storage of the samples in air for more than 3 days. The parent V-free materials were used as references.

3. Results

3.1. Macroscopic characteristics of the $\text{Si}\beta$ and $\text{Al}\beta$ zeolites

The dealumination did not introduce significant changes of the β architecture, as indicated by the similar X-ray diffractograms of the $\text{Al}\beta$ and $\text{Si}\beta$ samples (Fig. 1) and by the absence of any mesoporosity in the histograms of pore sizes of the two solids (not shown). However, a slight amorphization of the zeolite is suggested by a small decrease of its microporous volume (from $0.20\text{ cm}^3/\text{g}$ to $0.16\text{ cm}^3/\text{g}$). The determination of the β unit-cell parameters from powder diffractograms is known to be difficult due to the coexistence of the monoclinic and tetragonal polytypes [33]. A narrow diffraction peak, located near 22° – 23° , can however be used qualitatively to compare lattice contraction/expansion of the β structure within a given series of samples [34,35]. The d_{302} spacing related to this peak decreases from 3.9600 to about 3.9204

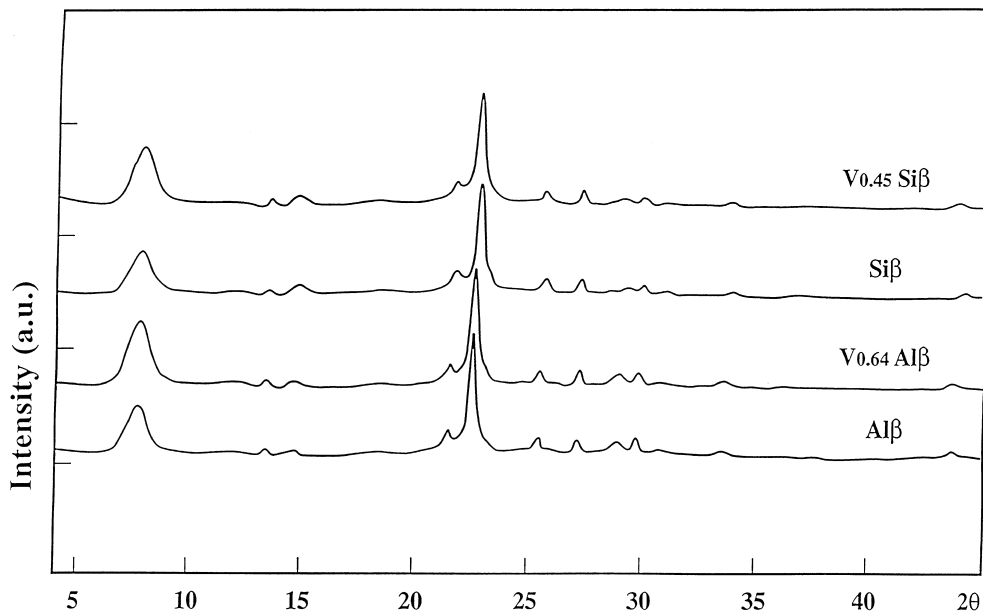


Fig. 1. X-ray diffractograms of the $\text{Al}\beta$, $\text{V}_{0.64}\text{Al}\beta$, $\text{Si}\beta$ and $\text{V}_{0.45}\text{Si}\beta$ samples.

Å upon dealumination, indicating some relaxation of the β matrix [25]. The dealumination also induces a significant shift of the FT-IR peak corresponding to the $\nu_{\text{As}}(\text{Si}-\text{O})$ vibrations, known to be sensitive to the chemical composition of the zeolite [36]. Observed at 1085 cm^{-1} for $\text{Al}\beta$, this $\nu_{\text{As}}(\text{Si}-\text{O})$ vibration is shifted to 1097 cm^{-1} for $\text{Si}\beta$ (Fig. 2A).

3.2. Microscopic characteristics of the $\text{Si}\beta$ and $\text{Al}\beta$ zeolites

At a microscopic level, the modifications induced by dealuminating the β matrix can be

directly investigated by FT-IR spectroscopy [31]. The FT-IR spectrum of $\text{Al}\beta$ exhibits the classical bands due to the hydroxyl vibrator of $\text{AlO}-\text{H}$ groups, at 3780 , 3662 and 3609 cm^{-1} (Fig. 2B) [31,37,38]. $\text{SiO}-\text{H}$ groups are also present, as indicated by a narrow peak at 3745 cm^{-1} , due to isolated silanol groups, and by a broad peak at 3530 cm^{-1} (full width at half maximum greater than 100 cm^{-1}), attributed to H-bonded $\text{SiO}-\text{H}$ groups [9,25,39,40]. Upon dealumination, the three bands attributed to $\text{AlO}-\text{H}$ groups are eliminated, confirming that the Al atoms are fully removed, and the intensity of the broad band of H-bonded silanol groups strongly in-

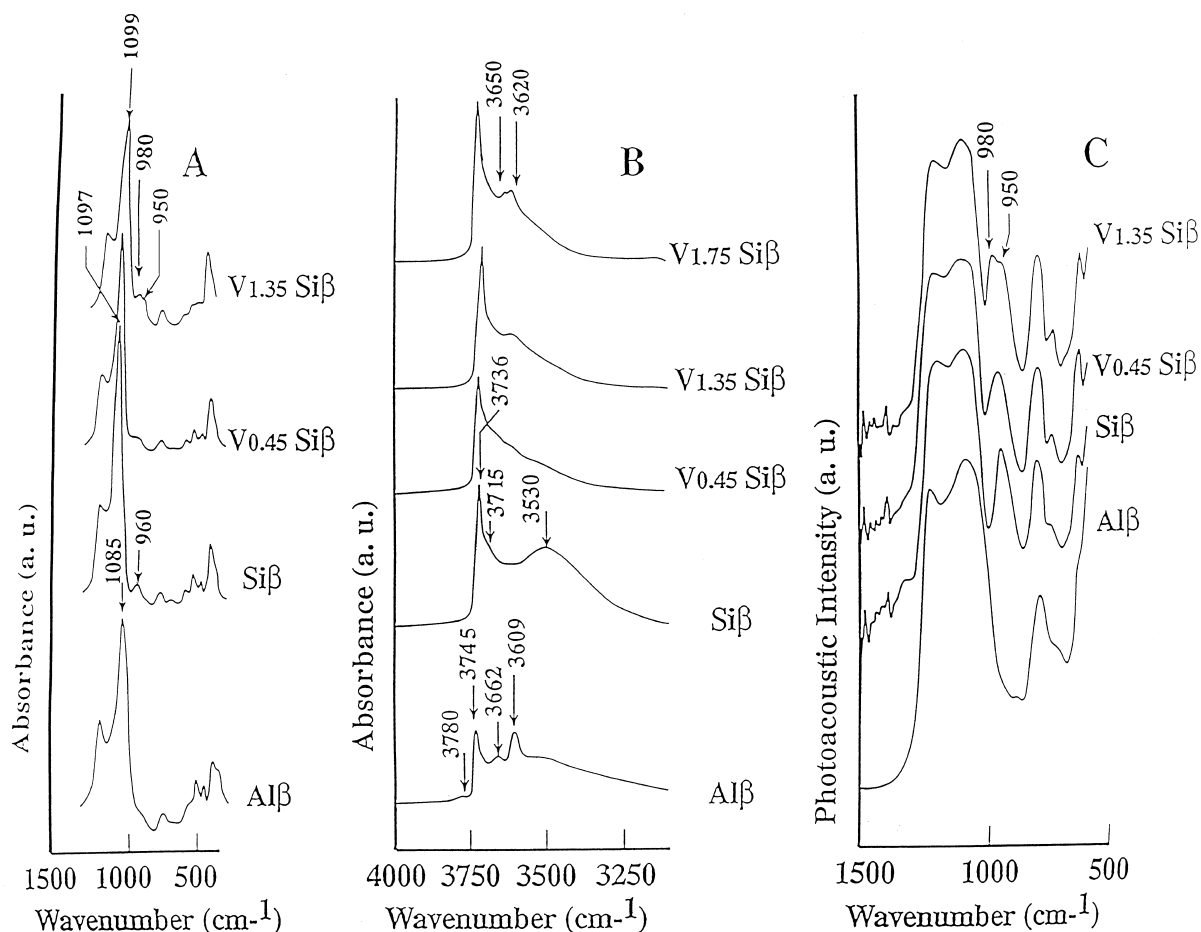


Fig. 2. FT-IR spectra of the $\text{Al}\beta$, $\text{Si}\beta$, $\text{V}_{0.45}\text{Si}\beta$, $\text{V}_{1.35}\text{Si}\beta$ and $\text{V}_{1.75}\text{Si}\beta$ samples: Transmission spectra in the spectral range of the Si-O stretching vibrations (A) and O-H stretching vibrations (B). Photoacoustic spectra (C). The intensities of the IR spectra have been normalized using the intensity of framework overtones located within the range $2000\text{--}1800\text{ cm}^{-1}$ (not shown) as internal standards.

creases (Fig. 2B). In parallel, the peak at 3745 cm^{-1} is replaced by a main peak at 3736 cm^{-1} and a shoulder at 3715 cm^{-1} . Similar features have already been observed on silica-based mesoporous MCM-41 materials and associated with two kinds of SiO–H groups, both experiencing no interaction via their H atoms [40]. The peak at 3736 cm^{-1} corresponds to isolated silanol groups, whereas, because of its lower position, the shoulder at 3715 cm^{-1} is associated with terminal SiO–H groups which oxygen interacts with the proton of a nearby hydroxyl group [40]. The presence of a large amount of silanol groups in Si β is confirmed by the intensity of a characteristic FT-IR peak near 960 cm^{-1} (Fig. 2A,C). Very weak with Al β , this peak is more intense with Si β , this difference being particularly visible when the FT-IR spectra are recorded with a photoacoustic detector (Fig. 2C). This peak, already observed for crushed silica, silica gels and various siliceous zeolites [41–46], has been assigned to the stretching vibration of Si–O vibrators belong-

ing to uncoupled (SiO $_4$) tetrahedra with a hydroxyl group. In our samples, we consider that this peak at 960 cm^{-1} reveals the presence of vacant T-sites associated with silanol groups generated upon dealuminating the β framework.

3.3. Macroscopic characteristics of the VAl β and VSi β zeolites

Chemical analyses of the VAl β and VSi β samples show that the number of V atoms per β unit cell increases when the initial concentration of V in the aqueous NH $_4$ VO $_3$ solution increases (Table 1, Fig. 3). However, for the same V content in the suspension, this number (and therefore the yield of V introduction also given in Table 1) is always lower in Al β . Thus, less than 50% of the V atoms of the suspensions are recovered in the VAl β solids whereas, up to a loading of 1.75 V atoms per unit cell, 100% are present in the VSi β samples. Moreover, the V atoms introduced in the VAl β samples are almost completely eliminated upon washing either

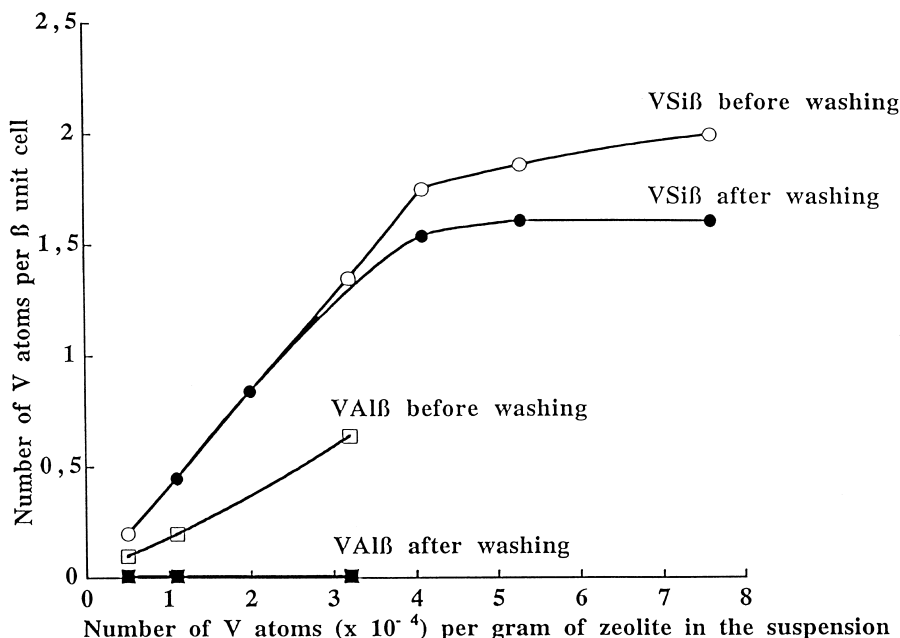


Fig. 3. Number of V atoms per β unit cell in the VAl β and VSi β samples, before and after washing in water and in NH $_4$ OAc aqueous solution, as a function of the number of V atoms per gram of zeolite in the initial NH $_4$ VO $_3$ suspensions.

in water or in an ammonium acetate aqueous solution whereas, up to the loading of 1.75 V atoms per unit cell, almost all V species are preserved in the VSi β samples; at higher loadings, the additional V species are removed (Fig. 3).

Whatever the parent Al β or Si β sample, both the β porosity and cristallinity are preserved upon V introduction. The diffractograms of the VAl β and VSi β zeolites do not show any evidence for neither the presence of non zeolitic crystalline compounds nor a long-range amorphization (Fig. 1), except for the V-richer V_{2.00}Si β sample (containing 2.6 wt.% of V) for which a slight decrease in intensity of the diffraction peaks is noticed (not shown). Moreover, for the VAl β samples, no significant change in the positions of the diffraction peaks is observed, indicating that the unit cell parameters of the β structure are not modified upon V introduction. In contrast, for the VSi β samples, the position of the main diffraction peak changes significantly as a function of the amount of V species. Up to 1.75 V atoms per unit cell, the d_{302} spacing value associated to this peak increases up to a constant value for greater amounts of vanadium (Fig. 4).

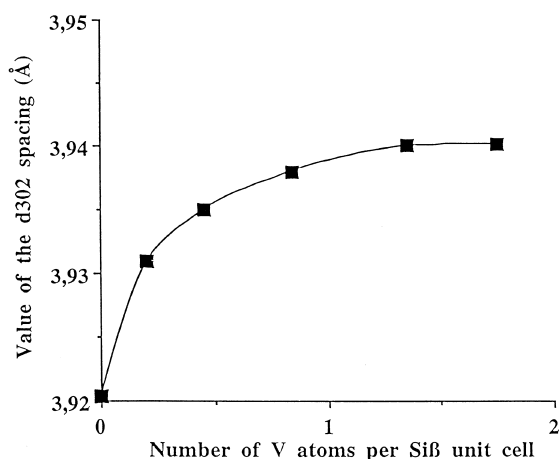


Fig. 4. Value of the d_{302} spacing associated with the most intense X-ray diffraction peak of β ($2\theta \sim 22^\circ$ – 23°) as a function of the number of V atoms incorporated per Si β unit cell.

3.4. Microscopic characteristics of the VAl β and VSi β zeolites

The introduction of V in the Al β zeolite did not induce any significant change of the FT-IR spectra (not shown) [25]. In contrast, strong differences exist between the spectra of the Si β and VSi β solids. Firstly, the intensity of the broad band near 3530 cm^{-1} , associated with hydrogen bonded silanol groups is significantly reduced upon V introduction, showing that silanol groups are consumed (Fig. 2B). Secondly, the aspect of the peak located near 960 cm^{-1} for Si β , assigned to silanol groups generated upon framework dealumination, is strongly modified in the presence of V with appearance of two maxima located at 950 and 980 cm^{-1} , clearly visible at high V loadings whatever the technique used to collect the spectra [in transmission (Fig. 2A) or using a photoacoustic detector (Fig. 2C)]. The appearance of these two resolved maxima clearly indicates that the silanol groups associated with vacant T-sites are modified upon introduction of the V species. Thirdly, two additional FT-IR peaks, respectively located at 3620 and 3650 cm^{-1} , are seen in the IR spectra of the dehydrated VSi β samples, particularly for large amounts of V (Fig. 2B).

To understand the origin of the two latter peaks, we have recorded the FT-IR spectra of pyridine adsorbed on the dehydrated Si β and VSi β samples (Fig. 5). On the dehydrated Si β , two bands at 1596 and 1445 cm^{-1} , characteristic of pyridine interacting with Lewis acid sites of silica-based matrices, are observed [47–49]. In the presence of vanadium, two additional bands, due to pyridinium cations [47–49], appear at 1544 and 1637 cm^{-1} which reveal that Brönsted-acid sites are formed. The formation of Brönsted-acid sites when V atoms are introduced in various siliceous zeolites has already been claimed from FT-IR studies of adsorption of ammonia [5,9]. However, the acidity of these V-loaded siliceous zeolites were not high enough to protonate pyridine [5]. In our samples, the

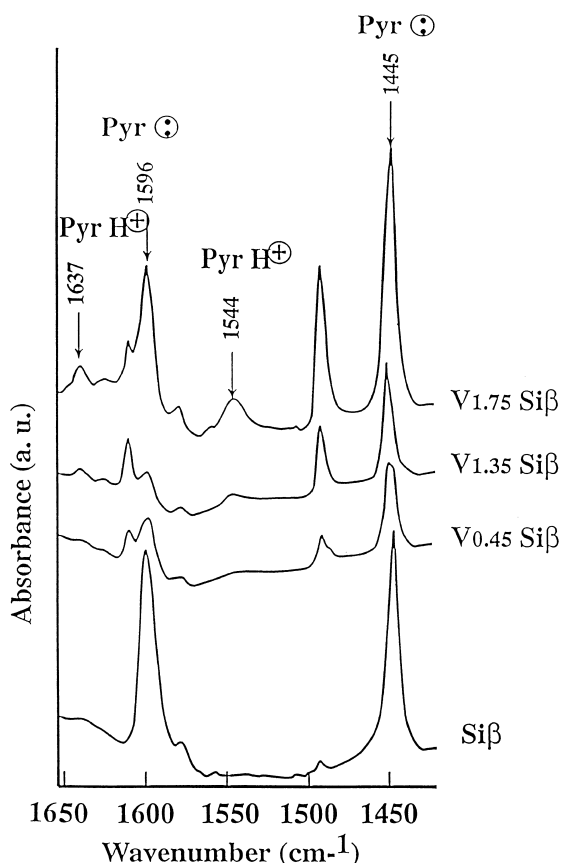


Fig. 5. FT-IR spectra of samples Si β , V $_{0.45}$ Si β , V $_{1.35}$ Si β and V $_{1.75}$ Si β after adsorption of pyridine (room temperature, 1 h) and evacuation (423 K, 1 h, 10^{-3} Pa).

intensity of the bands due to pyridinium ions increases with the V loading (Fig. 5) and a parallel progressive decrease of the intensity of the bands of OH at 3620 and 3650 cm^{-1} is observed. The last two OH bands are therefore associated with Brønsted-acid sites, able to transfer their proton to pyridine. The band at 3650 cm^{-1} , already observed for V supported on titania [50] and on titania/silica [51] materials can be assigned unambiguously to the hydroxyl vibrator of VO–H groups. The origin of the second band, located at 3620 cm^{-1} , is difficult to ascertain. Its lower position would however be consistent with an attribution to SiO–H groups experiencing strong SiO $^{\delta-} \cdots \delta^+ \text{V}$ interactions resulting in a Brønsted acidic character.

We have studied the environment of the V atoms in the VAl β and VSi β zeolites by diffuse reflectance UV–visible. The spectra of selected samples are compared in Fig. 6. Whatever the overall V amount, the absence of ($d-d$) transitions within the range 600–800 nm clearly indicates that no reduced V $^{\text{IV}}$ species have to be considered, oxidized V $^{\text{V}}$ species being mainly present [52,53]. For VAl β zeolites, a major, very broad absorption is observed near 415 nm. This band, already observed for various V-loaded siliceous materials, can be attributed to a low-energy charge transfer (CT) transition occurring between six oxygen ligands and a central V atom in a distorted octahedral coordination [5,27–30]. This band is not detected for the V $_{0.45}$ Si β sample for which two bands of similar intensities are observed at 270 and 340 nm

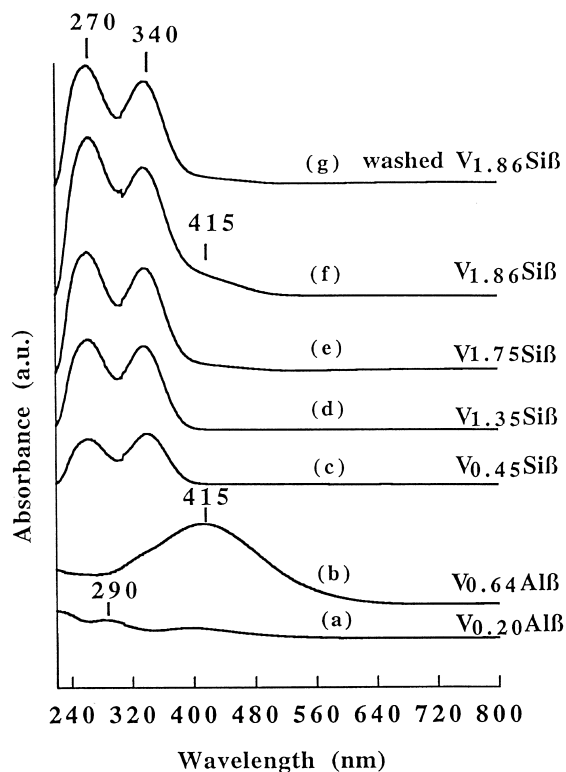


Fig. 6. UV–visible diffuse reflectance spectra of samples V $_{0.2}$ Al β (a), V $_{0.64}$ Al β (b), V $_{0.45}$ Si β (c), V $_{1.35}$ Si β (d), V $_{1.75}$ Si β (e) and V $_{1.86}$ Si β before (f) and after (g) washing with NH_4VO_3 . These spectra have been measured using Al β or Si β zeolites as references.

(Fig. 6c). These two bands have been reported for NH_4VO_3 and TlVO_4 in which V species are known to be surrounded by four oxygen ligands [5,27]. Similar bands have also been observed for various V-loaded silica-based materials [5,6,27–30,54] and associated with pseudotetrahedral $(\text{SiO})_3\text{V}=\text{O}$ species (also referred to $\text{O}_{3/2}\text{V}=\text{O}$ [27]) possessing a double $\text{V}=\text{O}$ bond and three single $\text{V}-\text{O}$ bonds. This assignment has been supported by photoluminescence [55,56] and ^{51}V solid-state NMR experiments [57]. Similar CT bands are observed in all the $\text{VSi}\beta$ samples but the band at 270 nm becomes progressively predominant as the amount of V increases (Fig. 6c–f). If more than 1.75 V atoms are introduced per unit cell, the absorption of octahedral V species becomes apparent near 415 nm (Fig. 6f). After washing treatments (Fig. 6g), the bands of the pseudotetrahedral $(\text{SiO})_3\text{V}=\text{O}$ species (two CT bands at 270 and 340 nm) are still present in the β solid whereas

the bands of octahedral V species (CT at 415 nm) are no longer identified.

As illustrated in Fig. 7, the presence of pseudotetrahedral $\text{O}_{3/2}\text{V}=\text{O}$ species in the $\text{V}_{1.75}\text{Si}\beta$ sample is confirmed by ^{51}V NMR spectroscopy. The MAS NMR spectrum of this sample has an isotropic chemical shift $\delta_{\text{iso}}(\text{MAS})$ of -633 ppm. Only a single set of side-bands is detected, indicating that one main kind of V species is present. The wide-line ^{51}V NMR spectrum, as established by its simulation ($\delta_{11} = -431$, $\delta_{22} = -559$ and $\delta_{33} = -750$ ppm), corresponds to a single line with an isotropic chemical shift δ_{iso} (static) equal to -580 ppm, a chemical shift anisotropy $\Delta\delta$ of -254 ppm and an asymmetry parameter, η , equal to 0.75. Similar spectral features have been reported with various V-loaded materials containing isolated V species in a distorted tetrahedral oxygen coordination [5,6,11,28–30,54,57]. The absence of any spectral contribution with a chemical shift at about $-300/-350$ ppm confirms that the $\text{V}_{1.75}\text{Si}\beta$ sample does not contain significant amounts of octahedral V species and is therefore vanadia-free [28,54,57,58].

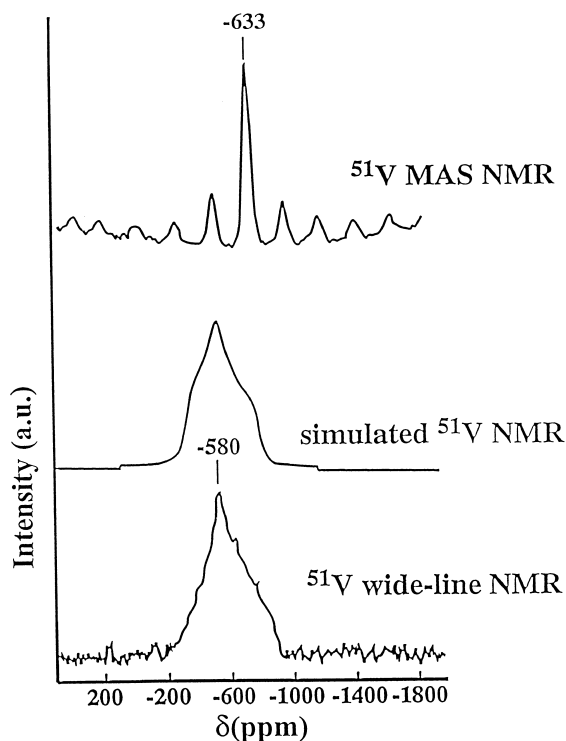


Fig. 7. 78.9 MHz ^{51}V wide-line NMR, simulated ^{51}V wide-line NMR and ^{51}V MAS NMR spectra of sample $\text{V}_{1.75}\text{Si}\beta$.

4. Discussion

The surface chemistry of silica-based matrices is known to be dominated by the presence of surface silanol groups, which can be used to attach transition metal species [59]. The present study provides interesting information on (1) the nature and reactivity toward ammonium metavanadate in aqueous solutions of the silanol groups present in nondealuminated and dealuminated β zeolite, (2) the nature of the V species formed upon introduction of V in the zeolite and the stability of these species toward washing treatments, (3) the nature of the bonding of the V species to the zeolitic walls.

4.1. Silanol groups in the $\text{Al}\beta$ and $\text{Si}\beta$ zeolites

Because of its defective nature (two polytypes, monoclinic and quadratic), silanols groups

are expected to be present in nondealuminated β zeolite [33]. Two different types of silanol groups are indeed detected by FT-IR in sample Al β (isolated and H-bonded silanol groups, characterized by O–H stretchings at 3740 and 3530 cm^{-1} respectively). After dealumination in a strong acidic medium, much larger amounts of silanol groups are present since the removal of framework Al generates vicinal silanol groups in vacant T-sites. The presence of such vacant T-sites in the Si β sample is associated with a characteristic FT-IR peak at 960 cm^{-1} , due to the Si–O stretching of uncoupled $[\text{SiO}_4]$ tetrahedra. Moreover, the larger amount of silanol groups in Si β than in Al β is consistent with ^{29}Si NMR results that we have already described elsewhere [25].

When the Al β sample is loaded with vanadium, no change is observed in the X-ray diffractograms or in the IR spectra. This suggests either that the V atoms which have been introduced in the solid do not interact strongly with the zeolitic walls or that the amount of strongly interacting V species is too small to generate noticeable modifications. In contrast, when the Si β zeolite is loaded with vanadium, significant changes of the β unit cell are observed which can be regarded as an indication of strong interactions between the zeolitic walls and the V species. This strong interaction is related to the presence of silanol groups which are consumed upon introduction of V, as revealed by the progressive disappearance of the IR bands of SiO–H vibrators at 3530 cm^{-1} .

The incorporation of V as species strongly interacting with the zeolitic walls also modifies the FT-IR peak of the silanol groups observed at 960 cm^{-1} in Si β , which is replaced in the VSi β samples by two distinct peaks at 950 and 980 cm^{-1} . Several authors have taken FT-IR peaks appearing around 960 cm^{-1} in silica-based matrices containing transition metal species, as an evidence for the isomorphous substitution of Si atoms by metal atoms [8,16,17,59]. Recently, Cambor et al. have attributed this peak in a Ti-loaded β zeolite to Si–OH defects, the con-

centration of which increases with the incorporation of Ti in framework position [60]. We assume similarly that the two maxima observed in VSi β samples are due to Si–O vibrators modified by the incorporation of V species within the β framework. Because of their positions, the two peaks at 980 and 950 cm^{-1} might be assigned respectively to Si–OV vibrator and to Si–O vibrator of silanol groups, polarized via interaction with vicinal V atoms ($\text{SiO}^{\delta-} \cdots \delta^+ \text{V}$).

4.2. Nature and stability toward washing of the V species

On the basis of characteristic UV–visible features, two kinds of structurally well-defined V species, namely octahedral (isolated and/or polymerized, CT band near 415 nm) and pseudotetrahedral $(\text{SiO})_3\text{V}=\text{O}$ (isolated, CT bands at 270 and 340 nm) V species are identified in the VAl β and VSi β zeolites.

4.2.1. Octahedral V species:

Less than 50% of the V atoms present in the initial suspensions are recovered in the VAl β zeolites. The VAl β samples are pale yellow and mainly characterized by a strong UV–visible absorption near 415 nm, typical of octahedral V species. This band is also found for the VSi β samples when more than 1.75 V atoms are introduced per unit cell. Upon washing treatments, the octahedral V species are removed from the solids indicating that the V atoms are loosely bound within the porosity of the zeolite. Washing in an ammonium acetate solution is generally proposed to eliminate the oligomeric metallic species trapped within the porosity of transition metal containing zeolites prepared by hydrothermal synthesis [5,8,14]. The same leaching effect is observed in our VAl β and VSi β samples when using either water or an ammonium acetate solution.

4.2.2. Pseudotetrahedral $(\text{SiO})_3\text{V}=\text{O}$ species

For less than 1.75 V atoms per unit cell, 100% of the V atoms present in the initial

aqueous suspensions are incorporated in the VSi β solids. These atoms are not removed upon washing in water or in NH₄OAc. UV–visible characterizations show that the V atoms are in pseudotetrahedral (SiO)₃V=O coordination and this attribution is confirmed by typical ⁵¹V NMR features. Even if they are distorted and cannot therefore be regarded as regular tetrahedral species, four independent observations suggest that these pseudotetrahedral (SiO)₃V=O species are incorporated within the vacant T-sites generated by dealuminating the zeolite: (1) their formation is associated with a progressive modification of the β unit cell parameters, indicating that the V species are homogeneously dispersed within the β matrix; (2) in their presence, the porosity of the β matrix remains accessible to N₂ molecules (BET); (3) the silanol groups generated upon dealumination are consumed when these pseudotetrahedral species are formed (progressive disappearance of the FT-IR peak at 3530 cm⁻¹ and modifications of the FT-IR peak at 960 cm⁻¹ as detailed above); (4) after washing treatments, the two intense CT bands of pseudotetrahedral (SiO)₃V=O species at 270 and 340 nm are still visible, showing that these species are strongly bound to the zeolitic walls.

Qualitatively, the pseudotetrahedral (SiO)₃-V=O species incorporated in the VSi β solids are comparable to the V species which have already been described: (1) grafted on the surface of silica and mesoporous matrices, (2) incorporated by hydrothermal treatment within various zeolites. However, in VSi β as in the latter materials, the pseudotetrahedral V species are stable in the presence of moisture whereas in grafted V-loaded materials, the coordination sphere of pseudotetrahedral V species is known to change spontaneously from four to six either by adding two water molecules or through oligomerization processes [27,28]. As observed for V-loaded zeolites [5,14] a specific local constraints or dispersion effects have therefore to be involved to explain the unsensitivity to water of the (SiO)₃V=O species evidenced in the present solids.

Quantitatively, the maximum amount of V atoms which are incorporated as pseudotetrahedral (SiO)₃V=O species resistant to washing in the VSi β zeolite (1.75 V atoms per unit cell) remains lower than the potential amount of framework vacant T-sites generated upon dealumination by removal of the framework Al atoms (5.3 Al atoms per unit cell). However, even an amount of 1.75 V atoms per unit cell is much higher (more than 20 times higher) than that usually reported for V-loaded zeolites prepared by direct synthesis in the presence of vanadium precursor [4–7]. Similarly, it is much higher than that incorporated in the VAl β samples (less than 0.1 V atoms per unit cell after washing). These differences in the yield of V incorporation indicate that, if the structural defects of nondealuminated zeolites participate to some extent to the incorporation of V atoms as pseudotetrahedral (SiO)₃V=O species, their contribution remains limited.

4.3. Nature of the bonding of the (SiO)₃V=O species to the zeolitic walls

The ⁵¹V NMR spectrum of the V_{1.75}Si β sample is comparable to spectra which have been reported for model V-containing silsesquioxane molecules, suggesting the presence of V as three-legged (SiO)₃V=O units [57]. However, the UV–visible spectra of the VSi β samples suggest that not only one type of pseudotetrahedral V species is present. Indeed, changes in the relative intensity of the two CT bands located at 270 and 340 nm are observed when the amount of V species changes and these changes might indicate the presence of more than one single type of pseudotetrahedral V species. Moreover, when the VSi β samples are dehydrated inside the cell, a FT-IR peak located at 3650 cm⁻¹ is observed which indicates that hydroxylated (SiO)₂(HO)V=O species are also present. Similar hydroxylated V species have already been reported for various V-loaded zeolites [4,5,8]. We propose thus that various amounts of non-hydroxylated (SiO)₃V=O and hydroxylated

$(\text{SiO})_2(\text{HO})\text{V}=\text{O}$ species might be stabilized within the $\text{Si}\beta$ matrix. This proposition would be consistent with photoluminescence data that we have presented earlier [56].

Another straightforward information from ^{51}V NMR spectroscopy is the smaller anisotropy of the chemical shift which characterizes the spectrum of the $\text{V}_{1.75}\text{Si}\beta$ sample as compared to that reported in the literature for pseudotetrahedral V species present within MCM-41 matrix [27]. Small anisotropies have already been reported for V-loaded ZSM-12 [13] and silicalite [4] and explained by considering (1) that vanadium may be connected to the lattice by only one or two oxygen bonds (such coordination allowing some mobility of the V atoms and therefore a decrease of anisotropy) [4,13] and (2) that hydrogen bonds may exist between SiOH groups and the oxygen of $\text{V}=\text{O}$ in $(\text{SiO})_3\text{V}=\text{O}$ units [13]. These two proposals are in line with our results which moreover suggest that two types of interactions may take place between the $\text{V}=\text{O}$ groups of the pseudotetrahedral $(\text{SiO})_2(\text{HO})\text{V}=\text{O}$ and $(\text{SiO})_3\text{V}=\text{O}$ species and the nearby SiOH groups, as illustrated in Fig. 8. Firstly, the oxygen of the $\text{V}=\text{O}$ group may interact, via H-bonding, with the proton of a nearby Si–OH group. Secondly, the incorporated V atom of the $\text{V}=\text{O}$ group may interact with a nearby donor group such as the oxygen of a Si–OH, leading

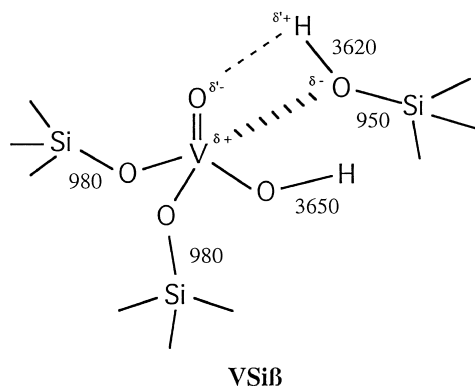


Fig. 8. Schematic representation of the interactions of the hydroxylated $(\text{SiO})_2(\text{HO})\text{V}=\text{O}$ species with a neighbour SiOH group; FT-IR stretching wavenumbers (cm^{-1}) of the various vibrators.

to a decreased π character of the $\text{V}=\text{O}$ double bond and therefore to an increased symmetry of the hydroxylated $(\text{SiO})_2(\text{HO})\text{V}=\text{O}$ species. The existence of such interactions would be consistent with FT-IR results. Indeed, in the dehydrated $\text{VSi}\beta$ samples, two FT-IR peaks, attributed respectively to O–H and Si–O stretching modes, are observed at 3620 and 950 cm^{-1} . These two peaks might indicate the presence of silanol groups polarized via $\text{H}^{\delta'+} \cdots \delta'^-\text{O}=\text{V}$ and/or $\text{Si}-\text{O}^{\delta-} \cdots \delta^+\text{V}$ interactions (Fig. 8) since their frequencies are significantly lower than the ones observed for silanol groups perturbed only by lateral interactions with nearby silanol groups (3715 and 960 cm^{-1}).

5. Conclusions

Remarkable differences are observed between samples prepared by contacting ammonium metavanadate solution with nondealuminated ($\text{Al}\beta$) and dealuminated ($\text{Si}\beta$) β zeolites. In the $\text{Al}\beta$, very low amounts of V atoms (less than 0.1 V atoms per unit cell), similar to those usually found in V-loaded zeolite prepared by hydrothermal synthesis, are incorporated by reacting with structural defects. In this zeolite, the V atoms are mostly introduced as octahedral V species which are easily extracted by washing with water or with an NH_4OAc solution. Owing to the high amount of silanol groups generated upon dealumination, much larger amount of V atoms are incorporated within $\text{Si}\beta$ (up to 1.75 V atoms per unit cell). As shown by UV–visible and ^{51}V NMR spectroscopies, the V atoms are incorporated as pseudotetrahedral V species, containing a $\text{V}=\text{O}$ double bond and linked by two $[(\text{SiO})_2(\text{HO})\text{V}=\text{O}$ species] or three $[(\text{SiO})_3\text{V}=\text{O}$ species] $\text{V}-\text{OSi}$ bounds to the zeolitic walls. The existence of hydroxylated $(\text{SiO})_2(\text{HO})\text{V}=\text{O}$ species, possessing a $\text{V}-\text{OH}$ group interacting with a nearby SiOH silanol group is supported by IR measurements (Si–O vibrators

at 950 and 980 cm^{-1} , O–H vibrators at 3620 and 3650 cm^{-1}). This interaction generates acidic Brønsted sites as shown by FT-IR in the presence of adsorbed pyridine.

Qualitatively, this work demonstrates the major importance of the silanol groups generated by dealumination toward incorporation of transition metal ions in zeolitic frameworks. It provides a convenient method for preparing metal-loaded zeolites in which the metal species are resistant to washing treatments. Quantitatively, this work shows that, in our experimental conditions (impregnation at room temperature, pH near 2.5), all the V atoms present in the impregnation suspension are incorporated in the dealuminated β framework up to a loading of 1.75 V atoms per unit cell. This V amount is lower than the potential amount of framework vacant T-sites generated by Al removal (5.3 per unit cell) but it is 20 times higher than that usually reported for V-loaded zeolite prepared by hydrothermal synthesis in the presence of vanadium precursor.

Acknowledgements

The Indo-French Center for the Promotion of Advanced Research (IFCPAR) is gratefully acknowledged for financial support under grant IFC 1006-1. Special thanks are due to B. Alonzo and J. Maquet (Laboratoire de Chimie de la Matière Condensée, UMR 7574-CNRS, Université Pierre et Marie Curie) for measuring the ^{51}V NMR spectra. A.D. gratefully acknowledges the Materials Research Laboratory (MRL, University of California at Santa Barbara) for the access to its photoacoustic FT-IR probe.

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