Incorporation of vanadium species in a dealuminated β zeolite

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V-loaded β zeolites can be prepared by a two-step post-synthesis method which consists of first creating vacant T-sites by dealumination of the β zeolite with nitric acid, then contacting them with an ammonium metavanadate solution; the SiOH consumption and the nature of the incorporated V species are characterized by IR, UV–VIS and ^{29}Si MAS NMR spectroscopies.

Transition metal cations can be efficiently dispersed in molecular sieves by using a two-step post-synthesis method.[1–3] The zeolite is first dealuminated with a strong acid (HCl, HNO_3, *etc.*) to generate vacant T-sites associated with silanol functional groups, which are then reacted with a highly reactive metallic precursor such as $TiCl_4$.[1,2] The procedures are often highly demanding, requiring both a perfectly anhydrous atmosphere and a high temperature (typically 673–773 K). The present work shows that a similar two-step method can be used to disperse vanadium species in a β zeolite even at room temp. using an aqueous solution as a V precursor.

A tetraethylammonium β zeolite (TEAβ) provided by RIPP (China) was separated into two fractions. The first fraction was calcined (12 h, 823 K) to obtain the non-dealuminated organic-free Hβ (Si/Al = 11). The second fraction was treated in a 13 M HNO_3 solution (4 h, 353 K) to give the dealuminated organic-free Siβ (Si/Al > 1300) used without further calcination. As already reported,[4] the dealumination does not affect the zeolite crystallinity of the β zeolite. The IR vibrations of the hydroxyls in these two solids are compared in Fig. 1(*a*). The three bands attributed to OH in Al–OH groups (3780, 3662, 3609 cm^{-1})[4,5] disappear after dealumination, confirming elimination of the Al atoms. Simultaneously, the intensity of several bands related to Si–OH groups increases (narrow bands of isolated silanol groups within the range 3700–3740 cm^{-1}, and a broad band of H-bonded SiOH groups centered near 3520 cm^{-1}).[6] Furthermore, a new IR peak is detected at *ca.* 960 cm^{-1} (not shown) which is assigned to uncoupled (Si–O) oscillators belonging to defective Si–OH groups.[7,8] ^{29}Si NMR spectroscopy confirms that stable silanol groups are generated by the dealumination. In all the spectra presented in Fig. 1(*b*) (MAS) and (*c*) (CP MAS), two main broad peaks, located at high field (δ −110 to −115) and downfield (δ −100 to −104) are observed. The high-field peak is due to framework Si atoms in a $Si(SiO)_4$ environment, located in different crystallographic sites.[9] For the non-dealuminated Hβ sample, the downfield peak is associated with Si atoms in $Si(OSi)_3(OAl)$ and $Si(OH)(OSi)_3$ environments.[4] The contribution from Si atoms associated with hydroxyl groups is revealed by the intense band which is detected at δ −102 when cross-polarization is applied. For the dealuminated Siβ sample, the downfield peak only corresponds to Si atoms in a $Si(OH)(OSi)_3$ environment. A small proportion of Si atoms in a $Si(OH)_2(OSi)_2$ environment is also evident (weak signal at *ca.* δ −91 in the cross-polarized spectrum of Siβ).[10]

Each sample (Hβ and Siβ) was contacted with an aqueous solution of NH_4VO_3 at 298 K (V/Si atomic ratio in the suspension within the range 0.007–0.021). Fig. 2(*a*) shows, as a function of time, the absorbance of the more diluted solution, measured at a constant wavelength of 380 nm, where the $O^{2-} \rightarrow V^{V}$ charge-transfer transitions are detected. With the Siβ zeolite, the absorbance decreases rapidly and disappears within a few hours indicating that the V ions initially present in the solution have reacted with the zeolite. With the Hβ sample, the absorbance rapidly reaches a non-zero constant value, showing that a non-negligible proportion of the V species

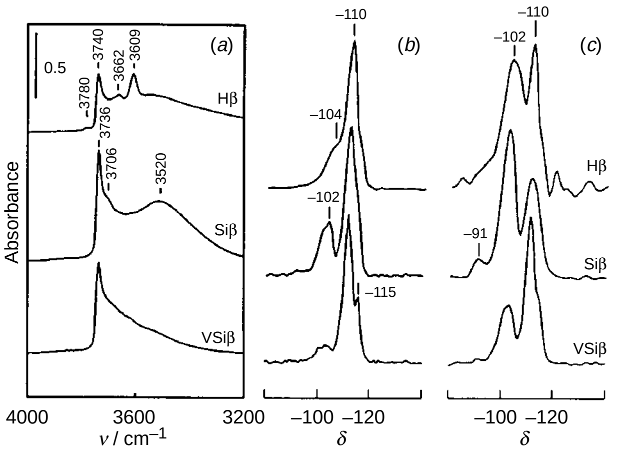

Fig. 1 (*a*) FTIR, (*b*) ^{29}Si MAS NMR and (*c*) ^{1}H–^{29}Si CP MAS NMR spectra of Hβ, Siβ and VSiβ samples (V/Si atomic ratio 0.007). The FTIR spectra were recorded on a Bruker IFS 66V FTIR spectrometer after calcination at 573 K (8 h, 120 ml min^{-1} O_2) and evacuation (10^{-5} Torr, 6 h) at the same temperature. The ^{29}Si NMR spectra were recorded on a Bruker MSL 400 at 79.5 MHz. The pulse length and recycle delay were 2.5 μs and 10 s respectively (MAS spectra). The proton π/2 pulse length, contact time, and recycle delay were 6.5 μs, 5 ms and 5 s, respectively (CP MAS).

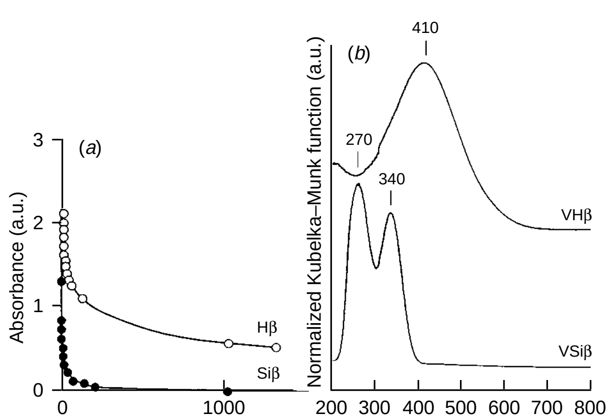

Fig. 2 (*a*) Evolution as a function of time of the UV–VIS absorbance measured at 380 nm on a 258 Ciba-Corning spectrometer, of an ammonium metavanadate solution (298 K, 7 × 10^{-4} mol l^{-1}) contacted with the Hβ and dealuminated Siβ samples (130 mg zeolite in 3 ml solution); (*b*) UV–VIS diffuse reflectance spectra of the VHβ and VSiβ zeolites (V/Si atomic ratios 0.013, 0.021 respectively), measured on a Cary spectrometer, using the parent V-free β zeolites as references.

remains in the solution, even after several days of contact with the non-dealuminated solid. The same trends have been observed using V solutions three times more concentrated.

After 3 days of contact with the solutions, the solids were recovered by centrifugation and dried overnight at 353 K. By chemical analysis, all the V species present in the initial solutions were detected inside the dealuminated VSiβ samples. By contrast, $< 60\%$ of the V species present in the initial solutions were found in the non-dealuminated VHβ solids. The VHβ samples were pale yellow whereas the VSiβ samples were white and their colour did not change even after several months in moist air. As indicated by Newsam *et al.*,[11] X-ray diffractograms of β materials are complex due to the intergrowth of a monoclinic and a quadratic polytype which makes unit-cell measurements difficult. For simplification, the *d*-spacings of single peaks indexed in a purely quadratic geometry are generally used to evidence lattice contraction and/or expansion.[12] On the non-dealuminated samples, no significant change in the d_{302} spacing was observed upon V incorporation ($< 0.1\%$). In contrast, the d_{302} spacing which has decreased from 3.960 (Hβ) to 3.920 Å (Siβ) upon dealumination, increases with increasing V loading in Siβ to reach a maximum value of 3.940 Å when the atomic V/Si ratio is 0.021. Because of the relative values of the Al–O, Si–O and V–O bond distances (1.790, 1.660 and 1.755 Å, respectively),[13] these variations strongly suggest that the vanadium species have been incorporated into the zeolite framework.

To obtain more information on the microstructure of the V sites, we have compared the diffuse reflectance UV–VIS spectra of V-loaded solids [Fig. 2(*b*)]. The absence of d–d transitions within the range 600–800 nm clearly indicates that no reduced V^{IV} species is formed, oxidized V^{V} species being mainly present.[14] For the VHβ sample, the major absorption located near 410 nm is due to a low-energy charge transfer transition occurring between octahedral oxygen ligands and a central V^{V} atom.[14,15] The spectrum of the VSiβ sample is different and exhibits two bands at 270 and 340 nm. associated with pseudotetrahedral $O_{3/2}V{=}O$ species, anchored to the zeolitic walls by three Si–O–V bridges and possessing a V=O double bond.[14–16]

Chemical analysis indicates that the octahedral V^{V} species detected in the VHβ samples are almost completely leached out by washing (12 h, 298 K) in a 1 M ammonium acetate solution. By contrast, the pseudotetrahedral species present in the VSiβ samples are strongly anchored to the zeolitic walls, $< 10\%$ of them being extracted by a similar washing. Furthermore, after incorporation of V on Siβ, the intensities of the broad IR band near 3520 cm^{-1} [Fig. 1(*a*)] and the downfield ^{29}Si MAS NMR peak at δ -102 [Fig. 1(*b*)] are significantly reduced, which confirms that a specific reaction takes place between the vanadium precursor and the silanol groups. Moreover, the aspect of the IR peak near 960 cm^{-1} is strongly modified with appearance of two maxima at 950 and 978 cm^{-1} as will be described elsewhere.

The catalytic behaviour of the VSiβ materials was tested in the oxidation of toluene in aqueous solution using H_2O_2 as an oxidant (molar ratio toluene/H_2O_2 = 3; 0.1 g of catalyst for 1 g of toluene).[17] After 9 h of reaction at 80 °C, toluene conversion was *ca.* 5% and the products distribution was 5–10% cresols, 85–90% benzaldehyde, 5% benzyl alcohol and benzoic acid.

In conclusion, catalytically active vanadium species can be easily dispersed within the porosity of a β zeolite using a two-step method. Because of its stacking faults, the β zeolite accepts a high density of silanols and depletion sites generated upon elimination of Al species. The silanol groups generated upon strong dealumination react with NH_4VO_3 aqueous solution, even at room temp., thus obviating the need for a highly reactive metallic precursor such as $VOCl_3$. Pseudotetrahedral and stable V^{V} species attached to the zeolitic walls are formed with the silanol-rich dealuminated sample, whereas loosely bonded octahedral V^{V} species are mostly generated when the non-dealuminated β is used instead. This clearly illustrates the role of the vacant T-sites and their associated silanol groups in the incorporation of vanadium species. To the best of our knowledge, this is the first time that vanadium species have been incorporated into a dealuminated β zeolite, which may be of importance in mild oxidation reactions that must be performed in the absence of strong acidity, as described by Corma and coworkers for Ti-β.[29]

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Footnotes and References

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