JOURNAL OF Materials CHEMISTRY

X-Ray absorption and photoelectron spectroscopic investigation of vanadium interaction with NH^{4+}- and Eu^{3+}-exchanged zeolite-Y following calcination and steam treatment

Lorenza Agasi,[b] Frank J. Berry,[a] Massimo Carbucicchio,[b] José F. Marco,[c] Michael Mortimer[a] and Frederic F. F. Vetel[a]

[a]*Department of Chemistry, The Open University, Walton Hall, Milton Keynes, UK MK7 6AA. E-mail: m.mortimer@open.ac.uk*
[b]*Dipartimento di Fisica, Università di Parma, and INFM, Parco Area della Scienze 71A, 43100 Parma, Italy*
[c]*Instituto de Química-Física 'Rocasolano', Consejo Superior de Investigaciones Científicas, c/Serrano 119, 28006 Madrid, Spain*

Received 7th June 2002, Accepted 12th July 2002
First published as an Advance Article on the web 2nd September 2002

X-Ray absorption near-edge structure, extended X-ray absorption fine structure and X-ray photoelectron spectroscopy have been used to investigate the interaction of vanadium with both NH^{4+}- and Eu^{3+}-exchanged, dealuminated zeolite-Y. In both cases, samples were subjected to either calcination or steam treatment at temperatures in the range 100 to 800 °C. Following deposition of vanadium, in the form of vanadyl(IV) acetylacetonate, there is evidence of a weak interaction between vanadium and the zeolite-Y framework. Under the conditions used in the work, treatment at increasing temperature, either in air or steam, results in the complete oxidation of V(IV) to V(V) at temperatures in the range 300 to 500 °C. At temperatures exceeding 500 °C, V(V) is present in tetrahedrally-distorted vanadium oxide species containing terminal V=O bonds, which are highly dispersed but bonded to the zeolite framework. These results show that the migration of vanadium into the zeolite-Y framework is not dependent on the presence of steam, nor is there any detectable influence of the exchanged Eu^{3+} cations.

Introduction

Modified variants of zeolite-Y have been extensively used in the petroleum industry as hydrocarbon cracking catalysts.[1–3] Important modifications to zeolite-Y have included exchange with rare earth cations and increasing the framework silicon-to-aluminium ratio by chemical or thermal dealumination processes.[4] These modifications, by themselves or in combination, enhance the hydrothermal stability and catalytic qualities of the zeolite-Y. However, it is well known[5–9] for all types of zeolite-Y that vanadium and nickel metal contaminants, which are present in crude oil as organometallic compounds such as porphyrins and naphthenates,[10–13] adversely affect catalytic performance. These compounds, and hence the metals, are continuously deposited on the surface of the catalyst, where they promote undesirable dehydrogenation reactions which increase coke and light gas production at the expense of gasoline yield. Vanadium, in addition, reduces catalytic activity and selectivity by destroying the crystallinity of the zeolite.[14]

The interaction of vanadium with zeolite-Y and, in particular, the mechanism by which the crystallinity of the zeolite is destroyed, has been the subject of a number of investigations,[5–9,14–16] although no overall consensus has been reached on the details of the processes involved. In recent work, Trujillo *et al.*,[14] in agreement with the earlier work of Pine,[15] have proposed that vanadium, in the form of vanadic acid, is involved in the destruction of the zeolite structure by framework hydrolysis.

In this work, we use X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and X-ray photoelectron spectroscopy (XPS) to investigate the location, coordination geometry and oxidation state of vanadium in both NH^{4+}- and Eu^{3+}-exchanged, dealuminated zeolite-Y treated with small amounts (*ca.*1.8% by mass) of vanadium. All measurements for both types of exchanged zeolite-Y were made at room temperature following, in each case, calcination or steam treatment at temperatures in the range 100 to 800 °C.

Experimental

The same commercial, dealuminated, ammonium-exchanged zeolite-Y was used as in previous work.[17] This was obtained from Zeolyst International (sample type CBV 712) and had minimal Na^+ content (0.03% by mass) and a bulk Si/Al molar ratio of 5.73. The framework value of the Si/Al molar ratio was found to be 13.5 ± 2.0 using standard ^{29}Si MAS NMR methods, although this ratio lies at the limit of reliability for the technique.[18] X-Ray powder diffraction showed the presence of a highly crystalline zeolite-Y phase with a unit cell parameter of 24.35 Å, which is typical for a dealuminated zeolite-Y.[19] MAS NMR measurements were made using a JEOL EX-400 spectrometer equipped with a 5 mm DOTY MAS probe and X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer in reflection mode using Cu-K_α radiation.

An Eu^{3+}-exchanged zeolite-Y was prepared by adding the commercial zeolite-Y to a 0.02 mol dm^{-3} aqueous solution of $Eu(NO_3)_3 \cdot 6H_2O$, followed by continuous stirring at around 60 °C and with pH *ca.* 3 over an extended period of time (24 h). The product was removed by centrifugation, washed with deionised water (60 °C, pH 3), filtered and dried in air at 60 °C (3 h). The ^{29}Si MAS NMR spectrum for the exchanged material was, within error, the same as that of the starting material.

DOI: 10.1039/b205533n

Vanadium was added to both the commercial zeolite-Y and the Eu^{3+}-exchanged zeolite-Y using a procedure based upon a variation of the approaches used by other workers.[14,15,20] Each material was added to a solution of vanadyl(IV) acetylacetonate [$VO(acac)_2$] in toluene, with the aim of obtaining 2% by mass vanadium deposition. The toluene solvent was removed in a rotary evaporator under vacuum. The europium and vanadium contents of the Eu^{3+}-exchanged zeolite-Y (V,Eu-z^Y) were determined by ICP analysis to be 4.17 and 1.78% (by mass), respectively. It is reasonable to assume that all of the europium is associated with the crystalline zeolite-Y since, throughout this and previous work,[17] no evidence was found for association between the amorphous material present in the zeolite and hydrated Eu^{3+} cations. On this basis, and assuming the MAS NMR value of the Si/Al molar ratio, the composition of the hydrated, crystalline V,Eu-z^Y was calculated to be $Eu_{4.25}(NH_4^+)_{0.25}Al_{13}Si_{179}O_{384}\cdot nH_2O$ (+ $V_{5.9}$), with minimal Na^+ content. There is essentially complete Eu^{3+} exchange and an Eu to V atomic ratio of approximately 1 : 1.4. The vanadium content of the NH_4^+-exchanged zeolite-Y (V-z^Y) was, within experimental uncertainty, equal to that for V,Eu-z^Y.

Calcination and steaming of individual samples of both V,Eu-z^Y and V-z^Y were carried out in a quartz tube, fiited with a sintered quartz plate, mounted in a vertical tube furnace.[21] Samples (typically 2 g) were heated at 5 °C min^{-1} to temperatures in the range 100 to 800 °C, and held for a period of 3 h. A flow of air (60 cm^3 min^{-1}) was sufficient to prevent any solid pellet formation. For steaming, samples were initially treated in the same manner as for calcination. However, once equilibriated at the set temperature, they were subjected to a flowing atmosphere (60 cm^3 min^{-1}) with a steam to air ratio of 80% for a period of 3 h. All samples were allowed to rehydrate in air after treatment and were investigated in air.

XANES and EXAFS measurements were performed at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory, Warrington, UK, operating at an energy of 2.0 GeV and an average current of 200 mA. Data were collected on Station 7.1 at 298 K using a Si(111) double-crystal, order-sorting monochromator in transmission mode. By detuning the crystals, 50% harmonic rejection was achieved. The energy scale was calibrated using a 6 μm vanadium foil. The position of the vanadium foil edge was taken as 5465.0 eV.[22] All the vanadium XANES data were referenced to this value. All the edges were recorded at least twice and at different times, separated by several hours, but within the lifetime of the beam. The edge profiles were separated from the EXAFS data and, after subtraction of the linear pre-edge background, normalised to the edge jump. The positions of the edges and the edge maxima were obtained from the maxima and zero points, respectively, of the first derivatives of the normalised edge profiles.[22] The reproducibility in the determination of the edge positions was found to be better than 0.2. eV. The EXAFS oscillations were isolated after background subtraction of the raw data using the Daresbury Laboratory program EXBACK and converted into k space. The data were weighted by k^3, where k is the photoelectron wavevector, to compensate for the diminishing amplitude of the EXAFS at high k. The data were fitted using the non-linear squares minimisation program EXCURV90.[23] The phase shifts were calculated using *ab initio* methods and tested on $VO(acac)_2$ and V_2O_5, the results being in good agreement with published data.[22]

XPS data were recorded with a Leybold Heraeus LHS-10 spectrometer under a vacuum of better than 1 × 10^{-8} Torr using Mg-K_α radiation and a constant analyzer transmission energy of 50 eV. All the spectra were recorded at a take-off angle of 90°. All binding energy values were charge corrected to the C 1s signal (284.6 eV). All the spectra were computer fitted and the binding energies are accurate to ±0.2 eV.

Results and discussion

X-Ray absorption spectroscopy

The XANES and EXAFS recorded from both the V-z^Y and V,Eu-z^Y samples as functions of temperature and of steam treatment were found to be indistinguishable within the experimental uncertainties. We illustrate our results with data recorded from the V,Eu-z^Y samples.

Fig. 1 shows the V *K*-edge X-ray absorption spectra recorded from original V,Eu-z^Y and from the same material subjected to calcination in the temperature range 100 to 800 °C. Similar results were obtained from the V,Eu-z^Y samples which underwent steam treatment in the same temperature range. Spectra for $VO(acac)_2$ and V_2O_5 are included in Fig. 1 as reference compounds. Pre-edge peaks are present in all of the spectra, which is characteristic of the behaviour found for a range of vanadium,[22,24] as well as other transition metal,[25–28] compounds. Table 1 provides a summary of the V *K*-edge XANES features for the spectra in Fig. 1 and, in addition, includes data for steamed V,Eu-z^Y samples.

The data recorded from the original V,Eu-z^Y are reasonably similar to those recorded from $VO(acac)_2$, and suggest that the

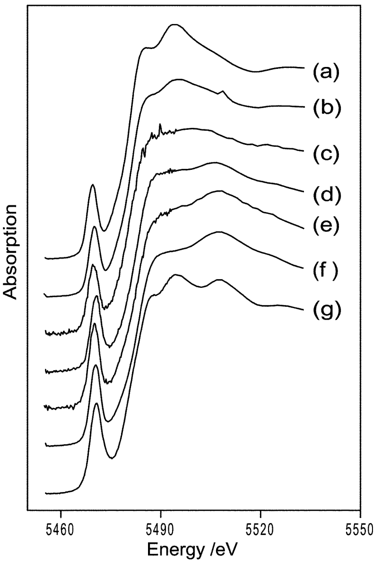

Fig. 1 Normalised V *K*-edge XANES recorded from (a) $VO(acac)_2$, (b) original V,Eu-z^Y, samples of V,Eu-z^Y calcined in air at (c) 100, (d) 300, (e) 600 and (f) 800 °C, and (g) V_2O_5.

Table 1 Vanadium *K*-edge XANES features recorded at room temperature[a]

	Pre-edge peak		Main edge	
Sample	Position/ eV	Intensity	Position/ eV	1s → 4p transition/eV
$VO(acac)_2$	4.6	0.37	15.9	18.6
V,Eu-z^Y	5.2	0.37	16.4	19.4
Calcined 100 °C	5.0	0.37	16.1	19.8
Steamed 100 °C	5.2	0.39	16.4	20.6
Calcined 300 °C	5.8	0.39	18.5	21.6
Steamed 300 °C	5.7	0.39	18.8	22.0
Calcined 600 °C	5.0	0.45	18.0	21.9
Steamed 600 °C	5.8	0.44	18.6	22.6
Calcined 800 °C	5.2	0.43	18.6	22.6
Steamed 800 °C	5.3	0.44	18.2	22.3
V_2O_5	5.6	0.45	17.3	29.5

[a] Energy positions are relative to the position of a 6 μm vanadium foil edge with, in most cases, estimated uncertainties of better than ±0.3 eV. Uncertainties in the positions of the 1s → 4p transition for V,Eu-z^Y samples heated to 100, 300 and 600 °C, in air or steam, increase to ±0.4 eV.

vanadium is initially present as V(IV) in similar coordination to that in the compound in which it was deposited. Treatment at increasing temperature, either in air or in steam, induces a shift to higher energy, particularly for the 1s → 4p transition, of the absorption features. This behaviour, taking into account the magnitudes of the observed changes, is typical of that for a unit change in the oxidation state of vanadium[22] and, as a consequence, we associate it with the oxidation of V(IV) to V(V). Within the heating regimes used, significant oxidation occurs on heating to 300 °C and oxidation is complete by 600 °C. These results are consistent with the conclusions drawn from the XPS studies (see later).

It is notable that there is a trend for the intensity of the pre-edge peak for V,Eu-z^Y to increase on heating, in either air or steam, at temperatures up to 600 °C. This pre-edge peak is due to transitions of the V 1s electron to final states that are essentially 3d states and the intensity is sensitive to the coordination geometry around vanadium.[22,25] In the specific case of perfect octahedral coordination, with a centre of inversion, the 1s → 3d transitions are Laporte forbidden and the pre-edge features are correspondingly very weak. In other geometries, such as square-pyramidal and tetrahedral, in which there is no inversion symmetry, pre-edge peaks are expected. These are due to dipole-allowed transitions to final states in which there is considerable mixing of V 3d and 4p orbitals as well as overlap with the orbitals of coordinating atoms; 2p in the case of oxygen.[24] In general, pre-edge peak intensities are greater for tetrahedral, as compared to square-pyramidal, coordination, although these intensities also vary according to the extent of distortions in these geometries. The observed changes in pre-edge peak intensity for V,Eu-z^Y on increasing thermal treatment, in air or in steam, indicate, at a qualitative level, that a change occurs in the coordination geometry around the vanadium atom as a function of treatment.

Vanadium *K*-edge EXAFS recorded at room temperature and their corresponding Fourier transforms are shown in Fig. 2 for V,Eu-z^Y samples following calcination treatment. The results obtained from the V,Eu-z^Y samples treated in steam were directly comparable.

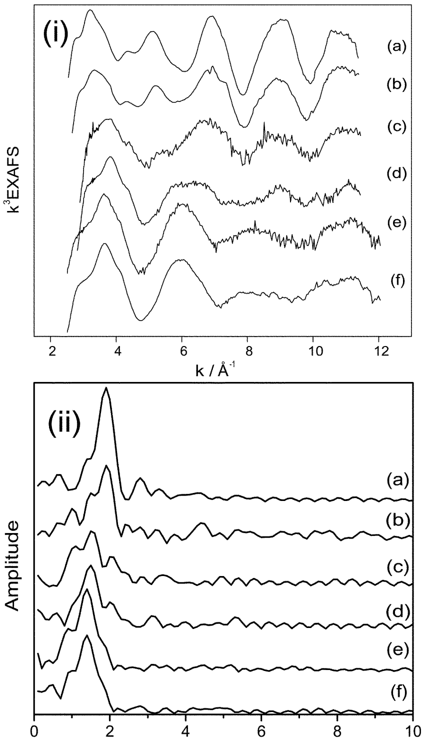

Fig. 2 k^3-Weighted V *K*-edge EXAFS (i) and the corresponding Fourier transforms (ii) recorded at room temperature from (a) $VO(acac)_2$, (b) original V,Eu-z^Y and V,Eu-z^Y samples calcined in air at (c) 100, (d) 300, (e) 600 and (f) 800 °C.

Table 2 Final fitted parameters obtained from V *K*-edge EXAFS data recorded at room temperature

Sample	Oxygen coordination number	r/Å (±0.02)	$2\sigma^2$/Å^2(±0.004)
$VO(acac)_2$	1	1.60	0.001
	4	1.97	0.012
V,Eu-z^Y	1	1.62	0.001
	4	1.95	0.023
Calcined 600 °C	1	1.61	0.001
	3	1.75	0.014
Steamed 600 °C	1	1.61	0.001
	3	1.75	0.016
Calcined 800 °C	1	1.62	0.004
	3	1.77	0.015
Steamed 800 °C	1	1.60	0.003
	3	1.74	0.010

The EXAFS recorded from the original V,Eu-z^Y were very similar to those recorded from $VO(acac)_2$, indicating that the distorted square-pyramidal geometry for vanadium did not change significantly following deposition onto the zeolite. This result is consistent with there being no change in the oxidation state of vanadium and is in agreement with the XANES data. The final fitted parameters to the data for $VO(acac)_2$ and original V,Eu-z^Y are given in Table 2. The Debye–Waller factor for the four equatorial oxygen atoms in the first coordination shell for vanadium in the original V,Eu-z^Y material is greater than that for the corresponding oxygen atoms in $VO(acac)_2$. This is reflected in the lower intensity of the EXAFS recorded from the original material and suggests some disorder within the first coordination shell, compatible with a loosely-bound, vanadium-containing species weakly interacting with the zeolite framework.

The EXAFS recorded from a sample following treatment in air or steam at 100 °C showed differences from that recorded from the original V,Eu-z^Y. These differences became even more evident for data recorded from samples treated at 300 °C. Overall, the EXAFS recorded at these latter temperatures may be considered as a combination of the results recorded from the original material and those heated at 800 °C in which only V(V) is present. This suggests that materials treated, in air or steam, in the region of 100 to 300 °C contain both V(IV) and V(V). This result is in agreement with the XANES data. It is also evident from Fig. 2 that the main peak in the Fourier transform of data recorded from materials heated at 600 and 800 °C shifts to shorter distances than that observed in data recorded from the original V,Eu-z^Y. Qualitatively, this is consistent with both a change in oxidation state of V(IV) to V(V) and with a change in coordination geometry of vanadium.

The EXAFS recorded following treatment of V,Eu-z^Y in air and steam at 600 and 800 °C were very similar. They were best fitted by a model (Fig. 3 and Table 2) in which V(V) has a distorted tetrahedral coordination to four oxygen atoms,[22] such that one of these oxygen atoms has a short vanadium–oxygen distance typical of that for a terminal V=O bond. In fact, the coordination geometry obtained is very close to that reported for vanadium species of the type $(Si–O)_3V=O$ in vanadium oxide catalysts supported on SiO_2,[29] and vanadium incorporated in zeolites with the ZSM-5[30] or silicalite (VS-2)[31] structures.

The increase in intensity observed in the 1s → 3d pre-edge feature of the XANES recorded from the V,Eu-z^Y samples following treatment, in air or steam, at increasing temperature may, therefore, be related to the changing site symmetry of the

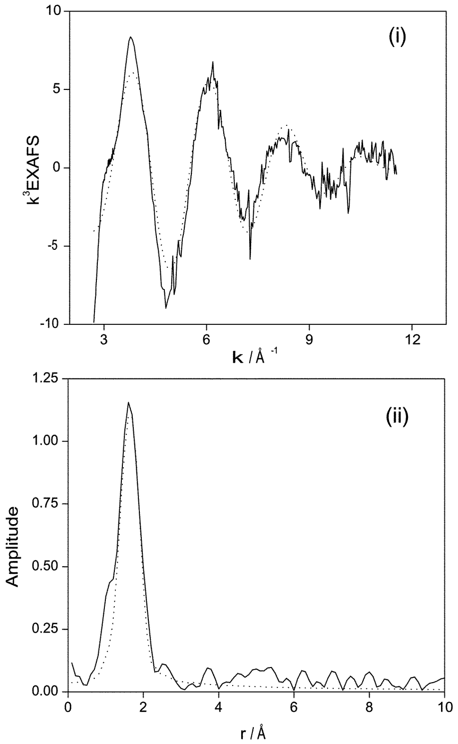

Fig. 3 k^3-Weighted V K-edge EXAFS (i) and the corresponding Fourier transform (ii) recorded at room temperature from V,Eu-z^Y treated in steam at 800 °C. The experimental data are indicated by solid lines and dotted lines indicate the best fit to the data.

vanadium atom from square-pyramidal in the original material to distorted tetrahedral in the samples treated at 600 and 800 °C. The absence of further peaks beyond 2 Å in the Fourier transform of the EXAFS data recorded from the samples treated at 600 and 800 °C suggests that the V(v) species are highly dispersed in the zeolite structure.[31] Overall, these results suggest, at least for the conditions of the present work, that the presence of steam is not essential for the migration and dispersal of vanadium into the zeolite structure. Furthermore, there is no detectable influence of the Eu^{3+}-exchanged cation on this process.

X-Ray photoelectron spectroscopy

The results recorded from the V-z^Y and V,Eu-z^Y samples as both a function of temperature and steam treatment were again very similar and are illustrated here by the data recorded from V-z^Y samples.

The binding energies of the main signals observed in the X-ray photoelectron spectra recorded from the commercial, dealuminated, NH_4^+-exchanged zeolite-Y (CBV 712), original V-z^Y and V-z^Y heated in both air and steam at 500 °C are collected in Table 3. The observed values for the Si 2p, O 1s and Al 2p peaks vary little from sample to sample and are within the range expected for a dealuminated zeolite-Y.[32–34] In general, these binding energies are expected to increase with increasing Si/Al molar ratio.[33] Overall, the results suggest that the binding energies of the core levels are not affected by either calcination or steam treatment. However, the V 2p$_{3/2}$ spectra recorded from the samples treated in air and steam at 500 °C show a clear shift to higher binding energy as compared to the V 2p$_{3/2}$ spectrum recorded from original V-z^Y. In order to obtain the binding energies of the V2p peaks, it was first necessary to fit the peaks corresponding to the O 1s $K_{\alpha3,4}$ X-ray satellites in the spectrum recorded from the vanadium-free, commercial zeolite-Y (two contributions located at 8.44 and 10.2 eV below the main O 1s signal). The positions, widths and area ratio obtained for these two peaks were then fixed during the fitting of the spectra recorded from the V-z^Y samples. The parameters used to define the spectral background were subsequently optimised and the final fits are shown in Fig. 4 and summarised in Table 3.

Table 3 Binding energies obtained from XPS recorded at room temperature

Sample	Si 2p/eV	O 1s/eV	Al 2p/eV	V 2p$_{3/2}$/eV, FWHM/eV
CBV 712	103.4	531.9	75.1	—, —
V-z^Y	103.3	531.7	75.1	515.5, 2.9
Calcined 500 °C	103.3	531.8	75.1	516.2, 2.9
Steamed 500 °C	103.4	531.9	75.1	516.2, 3.3

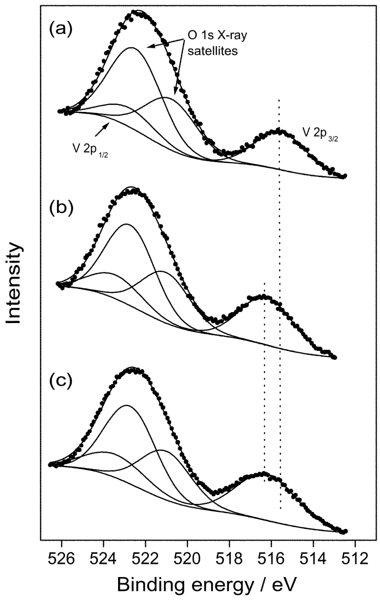

Fig. 4 O 1s $K_{\alpha3,4}$ X-ray satellites and V 2p X-ray photoelectron spectra recorded at room temperature from (a) original V-z^Y, (b) V-z^Y calcined at 500 °C, and (c) V-z^Y treated in steam at 500 °C. The positions of the O 1s satellites and the V 2p$_{1/2}$ and 2p$_{3/2}$ peaks are indicated.

The binding energy of the V 2p$_{3/2}$ core level obtained from the fit of the spectrum recorded from the original V-z^Y was 515.5 eV. We associate this value with the presence of V(IV) in VO^{2+}, as indicated by both XANES and EXAFS. This binding energy value is much lower than that recently associated with V(IV) in VO^{2+} in zeolite-Y (518.3–518.6 eV),[32] but it is close to the value reported for V(IV) in VO(acac)$_2$ (515.4 eV).[35] It is known that the dispersion of ions in a zeolite matrix leads to a considerable increase in the binding energies as compared to those observed in bulk materials.[32,36] Although this has usually been associated with metal cations in the corresponding oxide,[32] it should also be valid for oxo-cations such as VO^{2+}. Indeed, a similar effect has been found for vanadium-containing compounds on the surface of silica gel.[35] It appears that the support (either zeolite or silica gel) shows a strong electron-withdrawing effect and, correspondingly, the ionic character of surface-bound vanadium atoms are significantly increased. The results recorded here suggest that the vanadium species in the original V-z^Y must only be interacting very weakly with the zeolite framework; hence the relatively low binding energy. The XPS results agree well with those from EXAFS and XANES.

The V 2p X-ray photoelectron spectra recorded from V-z^Y treated in both air and steam at 500 °C are very similar. The binding energies of the V 2p$_{3/2}$ core levels determined from the fit of the spectra are, in both cases, 516.2 eV (Table 3). Thus, thermal treatment in either air or steam at 500 °C brings about an increase in the binding energy of the vanadium-containing species of *ca.* 0.7 eV. A similar binding energy has been reported for intra-zeolite V(v) oxide clusters, $(VO_{2.5})_x$, in which V(v) appears to be in distorted octahedral coordination.[32] In the present study, however, this cannot be the case, since both the EXAFS and XANES results indicate that the vanadium-containing species present in the samples treated at temperatures exceeding 300 °C corresponds to a V(v) species in a distorted tetrahedral coordination. It is interesting to note that the binding energy characteristic of isomorphously substituted V(v) in a distorted tetrahedral coordination is much higher (*ca.* 519.0 eV).[32] Therefore, the results presented here suggest that treatment in both air and steam at 500 °C does not induce the isomorphous substitution of aluminium or silicon by vanadium in the zeolite-Y framework. The binding energy of 516.2 eV is closer to that reported for V(v) surface compounds of the type $(Si–O)_3V=O$, $(Si–O)_3V$ or $(Si–O)_3V(O_2)$ (516.7, 516.0 and 516.4 eV, respectively).[35] If we take into account the XANES and EXAFS results, then the observed binding energy could well be associated with a framework surface species of the form $(Si–O)_3V=O$.

Conclusions

In this study, we have used a combination of XANES, EXAFS and XPS to monitor the changes in the local coordination and oxidation state of vanadium deposited in the form of $VO(acac)_2$ on a dealuminated zeolite-Y as a function of both heating in air and steam. Under all conditions, the interaction of the vanadium with the zeolite-Y framework was independent of whether the zeolite-Y was NH_4^+- or Eu^{3+}-exchanged. Our results are consistent with there being only a weak interaction between vanadium and the zeolite-Y framework following deposition. Heating in air, or steam, results in the oxidation of V(IV) to V(v), and this process, particularly in steam under the conditions used in the present work, may even occur at temperatures as low as 100 °C. Under the conditions used, only V(v) in a distorted tetrahedral coordination is present at temperatures above 500 °C. At these higher temperatures, the V(v) species is highly dispersed and is probably in the form of a framework surface species such as $(Si–O)_3V=O$. The presence of steam during heating, although probably beneficial, is not essential for promoting the migration and dispersal of vanadium throughout the zeolite-Y structure.

Acknowledgements

We thank EPSRC for beamtime at Daresbury Laboratory and BP Oil for financial support. The EU Socrates Programme is also thanked for financial support. We thank the Royal Society and the CSIC for the award of a travel grant (J. F. M.).

References

1 *Zeolite Chemistry and Catalysis*, ed. J. A. Rabo, ACS Monograph 171, American Chemical Society, Washington, DC, 1976.
2 C. N. Satterfield, *Heterogeneous Catalysis in Practice*, McGraw-Hill, New York, 1980.
3 B. W. Wojciechowski and A. Corma, *Catalytic Cracking Catalysts, Chemistry and Kinetics*, Marcell Dekker Inc., New York, 1986.
4 A. A. Avidan, *Akzo Catalysts Symposium: Fluid Catalytic Cracking*, ed. B. van Kealen, Akzo Chemical Division, Amersfoot, The Netherlands, 1991.
5 S. Jaras, *Appl. Catal.*, 1982, **2**, 207.
6 R. F. Wormsbecher, A. W. Peters and J. M. Maselli, *J. Catal.*, 1986, **100**, 130.
7 M. L. Occelli, *Catal. Rev. Sci. Eng.*, 1991, **33**, 241.
8 M. Torrealba, M. R. Goldwasser, G. Perot and M. Guisnet, *Appl. Catal,. A*, 1992, **90**, 35.
9 J. S. Magee and M. M. Mitchell Jr., *Stud. Surf. Sci. Catal.*, 1993, **76**, 105.
10 P. Sundararaman, *Anal. Chem.*, 1985, **57**, 2204.
11 J. E. Otherstedt, S. B. Gevert, S. G. Jaeras and P. G. Menon, *Appl. Catal.*, 1986, **22**, 159.
12 P. C. H. Mitchell and C. E. Scott, *Polyhedron*, 1986, **5**, 237.
13 H. Knözinger, D. Cordischi and B. Vielhaber, *Catal. Today*, 1990, **7**, 447.
14 C. A. Trujillo, U. N. Uribe, P. P. Knops-Gerrits, L. A. Oviedo and P. A. Jacobs, *J. Catal.*, 1997, **168**, 1.
15 L. A. Pine, *J. Catal.*, 1990, **125**, 514.
16 G. L. Woolery, A. A. Chin, G. W. Kircher and A. Huss Jr., *ACS Symp. Ser.*, 1988, **375**, 215.
17 F. J. Berry, M. Carbucicchio, A. Chiari, C. Johnson, E. A. Moore, M. Mortimer and F. F. F. Vetel, *J. Mater. Chem.*, 2000, **10**, 2131.
18 J. Klinowski, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1984, **16**, 237.
19 J. Klinowski, C. A. Fyfe and G. C. Gobbi, *J. Chem. Soc., Faraday Trans.*, 1985, **81**, 3003.
20 B. R. Mitchell, *Ind. Eng. Chem. Prod. Res. Dev.*, 1980, **19**, 209.
21 J. S. Sarginson, *PhD Thesis*, Open University, 1997.
22 J. Wong, F. W. Lytle, R. P. Messmer and D. H. Maylotte, *Phys. Rev. B*, 1984, **30**, 5596–5610.
23 N. Binsted, S. Gurman and J. Campbell, EXCURV90, CCLRC, Daresbury Laboratory, Warrington, UK, 1990.
24 T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki and S. Yoshida, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 2987.
25 R. G. Shulman, Y. Yafet, P. Eisenberger and W. E. Blumberg, *Proc. Natl. Acad. Sci. U. S. A.*, 1976, **73**, 1384.
26 S. Bordiga, S. Coluccia, C. Lamberti, L. Marchese, A. Zecchina, F. Boscherini, F. Buffa, F. Genoni, G. Leofanti, G. Petrini and G. Vlaic, *J. Phys. Chem.*, 1994, **98**, 4125.
27 A. Moen, D. G. Nicholson and M. Rønning, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3189.
28 A. Moen, D. G. Nicholson, M. Rønning, G. M. Lamble, Jyh-Fu Lee and H. Emerich, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 4071.
29 M. Anpo, in *Handbook of Heterogeneous Catalysis Volume 2*, ed. G. Ertl, H. Knözinger and J. Weitkamp, Wiley-VCH, Weinheim, 1997, p. 664.
30 S. G. Zhang, H. Higashimito, H. Yamashita and M. Anpo, *J. Phys. Chem., B*, 1998, **102**, 5590.
31 M. Anpo, S. G. Zhang, H. Mishima, M. Matsuoka and M. Yamashita, *Catal. Today*, 1997, **39**, 159.
32 M. Wark, M. Koch, A. Brückner and W. Grünert, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2033.
33 C. D. Wagner, D. E. Passoja, H. F. Hillery, T. G. Kinisky, H. A. Six, W. T. Jansen and J. A. Taylor, *J. Vac. Sci. Technol.*, 1982, **21**, 933.
34 A. Kazlov, K. Asakura and Y. Iwasawa, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 809.
35 B. Hovarth, J. Strutz, J. Geyer-Lippmann and E. G. Hovarth, *Z. Anorg. Allg. Chem.*, 1981, **483**, 181.
36 M. Wark, A. Brückner, T. Liese and W. Grünert, *J. Catal.*, 1998, **175**, 48.