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Characterisation by vibrational and electronic spectroscopies

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Abstract

The EUROCAT SCR catalyst has been characterised by IR spectroscopic methods (transmission/absorption and diffuse reflectance techniques) by investigating its spectrum after different outgassing treatments, and the spectra of the surface species arising from adsorption of water (surface hydroxyl groups), carbon monoxide, ammonia, pyridine, nitrogen monoxide, trimethyl borate and $NO + NH_3$ coadsorptions. Additionally, Raman spectra and DR UV–Vis spectra have been reported after different outgassing treatments. The presence of Lewis and Brønsted acid sites has been discussed, as well as the evidence of different electronic states. A picture for the surface structure of the catalyst has been obtained. This picture is not significantly modified after extensive use of the catalyst in an SCR reactor for denitrifaction of flue gases from an incineration plant. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: IR; Raman; DR UV–Vig spectroscopies; Denitrifaction; EUROCAT oxide

1. Introduction

The SCR process is a very efficient heterogeneous environmental catalytic process allowing the denitrification of very different kinds of flue gases down to very low NO_x concentrations. The technological [1] and chemical and mechanistic features [2] of this process have been recently reviewed extensively. However, little data have been reported in the literature concerning real industrial catalysts. Recently, a paper has been published reporting the spectroscopic characterisation of a commercial catalyst applied to the denitrification of As-poor waste gases from power plants [3]. No other detailed characterisation studies have been published, to our knowledge, concerning the structural and surface characterisation of SCR catalysts intended for other applications. Upon the EUROCAT SCR program a catalyst intended for application in incinerator plants has been characterised by several different groups. The results of this comprehensive study are reported here, showing also the good agreement between the data obtained in different laboratories with similar techniques.

2. Experimental

IR spectra were obtained with the following Fourier-transform (FT) instruments: Bruker IFS22 (Laboratory F-1), IFS66 (Laboratory D-1) and IFS48 (Laboratory I-2), Nicolet 5ZDX (Laboratory E-1) and Protege 460 (Laboratory I-1), Perkin-Elmer 16PC (Laboratory E-2), all in the transmission mode, and

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with Perkin-Elmer 1600 equipped with a Graseby Specac controlled environment cell (Laboratory PT-1) in the diffuse reflectance mode.

Raman spectra were obtained with Perkin-Elmer 1700 X (1064 nm exciting radiation, 0.25–0.5 W power, Laboratory GB-1) and Bruker RFS 100 (Nd-YAG Laser, Laboratory E-1) FT-Raman instruments.

UV–Vis diffuse reflectance spectra were obtained with Jasco V-570 (Laboratory I-1), Perkin-Elmer Lambda 19 (Laboratory I-2), Shimadzu UV 240 (Laboratory E-2) and UV-2100 (Laboratory E-1) instruments, equipped with conventional integrating spheres.

3. Results and discussion

3.1. Skeletal vibrational spectra

Infrared skeletal spectra of the samples were obtained by the KBr pressed disk technique in different laboratories (E-1, E-2, F-1). For the sake of brevity, only the data obtained by the E-1 group will be presented. The spectrum of the fresh catalyst is dominated by a band centred at 633 cm^{-1} with a shoulder at 536 cm^{-1} (Fig. 1a), which is slightly shifted to higher frequency with respect to the spectrum of the TiO$_2$ used as support in the previous work [4]. Additional components are found at higher frequency; in particular a quite sharp and intense doublet is found at 1102 and 1073 cm^{-1}, with a weak component at ca. 980 cm^{-1}. The doublet is likely associated with Si–O–Si asymmetric stretchings of silica or silicate particles which are known to be mixed with real SCR catalysts to improve the mechanical strength and resistance to erosion. The weak band at ca. 980 cm^{-1} could be due either to V=O or W=O stretchings [5,6].

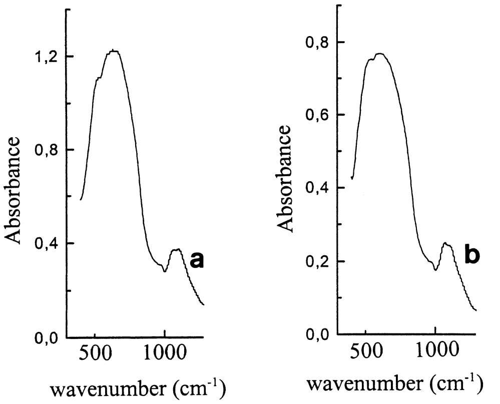

Fig. 1. FTIR spectra of KBr pressed disks of the fresh (a) and used (b) EUROCAT SCR catalyst (Laboratory E-1).

Essentially the same features were observed in the case of the used catalyst, with only minor changes in the relative intensity of the various spectral components (Fig. 1b).

Finally, similar results for both the fresh and used catalysts were obtained by the PT-1 group by using diffuse reflectance FTIR spectroscopy, although the observed absorptions appeared less well resolved.

The Raman spectra of the fresh and used catalysts have been recorded by the E-1 and GB-1 groups using FT-Raman instruments (Fig. 2). In both cases the strong Raman peaks of anatase are observed at 148 (maximum out of scale in the figure), 394, 513 and 636 cm^{-1}, with a weak shoulder at 199 cm^{-1} and a weak component at ca. 800 cm^{-1}, also due to anatase. These peaks were observed by the GB-1 group also by recording the spectrum of the used and fresh catalysts in the form of monolith fragments, without grinding. The E-1 group observed other weaker bands at 280, 570 (broad) and 700 cm^{-1}, which, according to these authors, could indicate traces of highly dispersed WO$_3$ phase. An additional broad feature with a sharp maximum at 993 cm^{-1} was observed by using both Raman instruments. This component could be due to V=O or W=O stretchings [5,6].

Raman spectroscopy did not show significant differences between the fresh and used catalysts.

3.2. Electronic spectra

Diffuse reflectance UV–Vis spectra of the fresh and used catalysts in air were obtained by the E-1 and E-2 laboratories, while the I-1 and I-2 groups recorded also the spectra of the samples thermally treated in various ways. Fig. 3 reports the spectra, recorded by the I-2 laboratory, of the bare support outgassed and re-oxidised at 623 K (curve a) and of the fresh catalyst treated in the same conditions (curve b) and then rehydrated by contact with water vapour (curve c). The spectrum of the support simply exhibits a

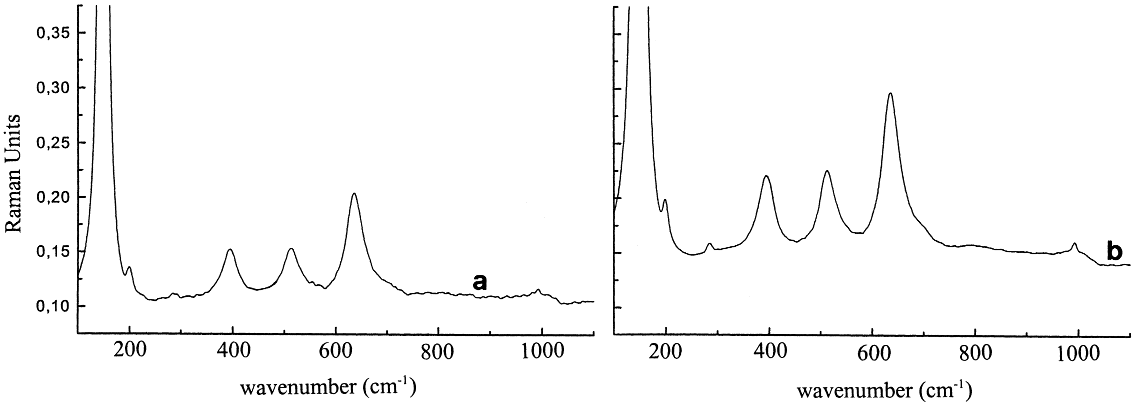

Fig. 2. FT-Raman spectra of the fresh (a) and used (b) EUROCAT SCR catalyst (Laboratory E-1).

strong edge above 25 000 cm^{-1}, characteristic of the valence to conduction band transition, arising from O^{2-} 2p→Ti^{4+} 3d charge transfer transition [7]. XPS measurements and chemical analyses indicated that the support is actually a binary WO_3/TiO_2 system, and then the edge at ca. 25 000 cm^{-1} could be partly due to O^{2-} 2p→W^{6+} 5d charge transfer transition in WO_3-like structure [8]. In the case of the dehydrated catalyst, an additional broad absorption is observed in the 29 000–18 000 cm^{-1} range, zeroing at ca. 13 000 cm^{-1} (Fig. 3b), due to electronic transitions involving V^{5+} ions dispersed on the WO_3/TiO_2 support. A part of this feature appears sensitive to the hydration state of the surface. In fact, by admitting water vapour onto the catalyst a slight depletion of the absorption in the 29 000–24 000 cm^{-1} range occurs, while a parallel slight increase in intensity of the signal is observed in the 22 000–18 000 cm^{-1} region (Fig. 3c).

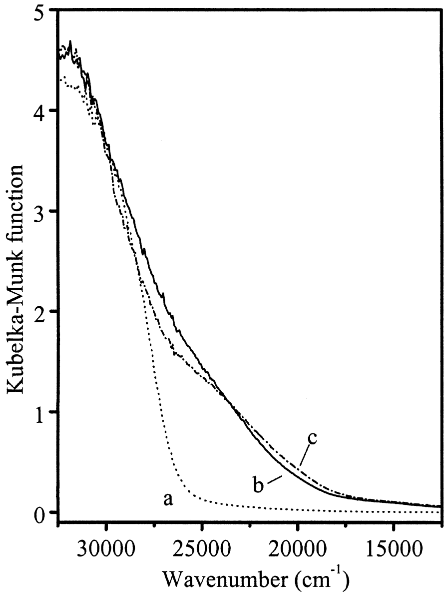

Fig. 3. Diffuse reflectance UV–Vis spectra of the bare support (a) and of the fresh EUROCAT SCR (b) outgassed at 623 K for 1 h and re-oxidised at the same temperature (see Section 2). Curve c is the spectrum of such activated EUROCAT SCR catalyst contacted with 18 Torr water vapour (Laboratory I-2).

On the basis of literature data on reference compounds or model supported vanadia catalysts [9,10] the bands observed in the studied spectral range can be assigned to O^{2-} 2p→V^{5+} 3d charge transfer transitions involving V^{5+} ions in pseudo-tetrahedral (p-T_d) ligand field in clusterised structure (29 000 cm^{-1}), V^{5+} species in square-pyramidal coordination (S_p) in two-dimensional layers (25 000 cm^{-1}) and V^{5+} ions in a distorted octahedral coordination in three-dimensional V_2O_5-like species (21 000 cm^{-1}). The presence of such agglomerated structures in the studied catalyst could be explained on the basis of the relatively high V_2O_5 loading with respect to the specific surface area of the support. Moreover, it may be considered that a fraction of the TiO_2 surface should be occupied by the W containing species, and this should further reduce the dispersion of the vanadia phase.

The effect observed by rehydration of the catalyst should be mainly due to the conversion of V^{5+} ions in pseudo-tetrahedral ligand field into pseudo-octahedral V^{5+} species by adsorbing two water molecules. This feature confirms the attribution of the part of the absorption near 29 000 cm^{-1} to surface p-T_dV^{5+} ions. Furthermore, also V^{5+} species in S_p coordination could be converted into pseudo-octahedral structures by adsorbing one H_2O molecule. However, the component near 25 000 cm^{-1} is only very slightly affected by the admission of water. This suggests that multilayer two-dimensional patches containing V^{5+} in S_p coordination are actually present, only the minor fraction of such sites exposed at their surface being accessible to water. Finally, the weak tail in the 16 000–13 000 cm^{-1} range observed in both the dehydrated and hydrated form of the catalyst (Fig. 3b,c) should be attributed to the d–d transition of V^{4+} ions [11].

The effect of the simple outgassing at increasing temperature on the electronic spectra of the catalyst has been studied by both I-1 and I-2 laboratories. The spectra recorded by the I-2 group show that in the case of the WO_3/TiO_2 support (Fig. 4A) such treatment causes the appearance of a new edge-like absorption with the onset near 10 000 cm^{-1} and the maximum intensity below 20 000 cm^{-1}. As is well known [12] this feature is due to the promotion of nearly free electrons in the conduction band, arising from the partial reduction of titania and tungsta occurring through oxygen loss during the outgassing.

The behaviour of the fresh catalyst is shown in Fig. 4B. In this case a new absorption is also found in the 10 000–22 000 cm^{-1} range, but exhibiting a band-like more than edge-like shape. Additionally, a decrease of the absorption due to the O 2p→V^{5+} 3d charge transfer transition is observed. This behaviour is interpreted as due to the reduction of V^{5+} to V^{4+}, resulting in localised (at room temperature) reduced centres characterised by d–d transition in the visible region [11].

Similar measurements were carried out on the used catalyst, and essentially the same results were obtained.

3.3. FTIR spectra of catalyst surface species

FTIR spectra of the species present on the surface of the catalysts were obtained by the F-1, I-1 and I-2 groups by using self-supporting pellets of the samples. The FTIR spectra, recorded in the I-2 laboratory,

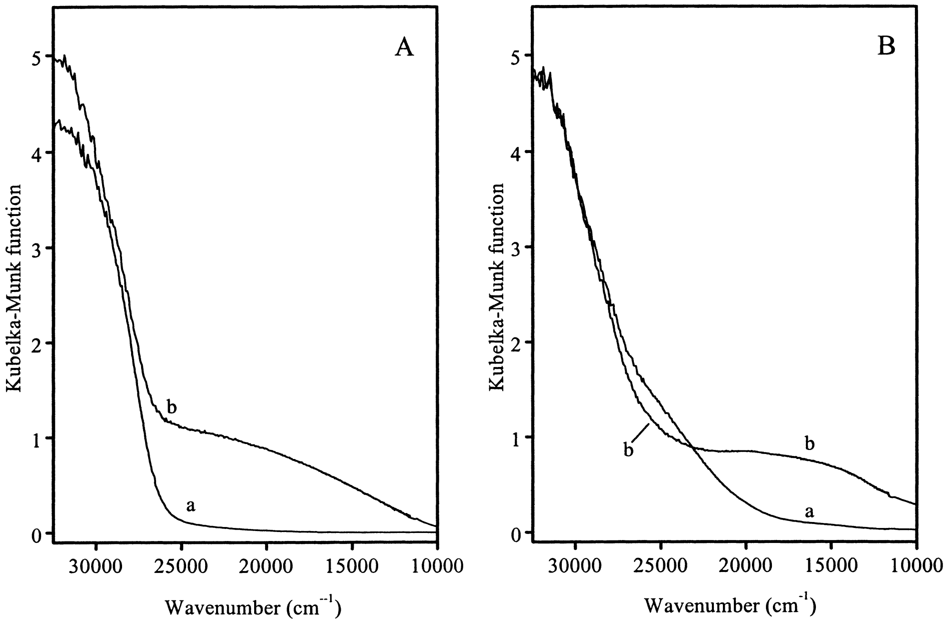

Fig. 4. Diffuse reflectance UV–Vis spectra of the WO_3/TiO_2 support (section A) and of the fresh EUROCAT SCR catalyst (section B) outgassed at room temperature (curves a) and at 623 K (curves b) (Laboratory I-2).

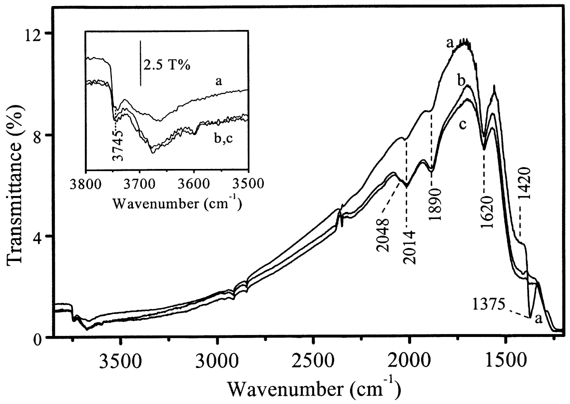

Fig. 5. FTIR spectra (self supporting pellets) of the TiO_2 support and of the fresh (b) and used (c) EUROCAT SCR catalyst outgassed at 623 K for 1 h and re-oxidised at the same temperature (see Section 2) (Laboratory I-2).

of the bare support and of the fresh and used catalysts outgassed and re-oxidised at 623 K are shown in Fig. 5a–c. In all cases, the cut-off limit, found near 1250 cm^{-1}, is located at much higher frequencies with respect to that which was observed on “model” SCR catalysts, near 1000 cm^{-1} [13], because of the Si–O stretching absorption associated with silica particles mixed with the catalyst particles. Near 1890 cm^{-1} a broad absorption due to overtone and combination of these skeletal vibrations is also detectable. The siliceous phase is also responsible for the 3745 cm^{-1} band observed in the high frequency region of all three samples, due to the OH stretching of surface silanol groups ([14], Fig. 5 inset).

A strong peak is observed at 1375 cm^{-1} in the spectrum of the WO_3/TiO_2 support (Fig. 5a). This band, previously observed, although with higher intensity, on other commercial catalysts [3] is typical of surface sulphate species on sulphated TiO_2-anatase after outgassing and drying, and is assignable to the S=O stretching mode of tricoordinated sulphate ions [15]. This absorption appears strongly reduced in intensity for both the fresh and used catalysts (Fig. 5b and c).

In all cases, other bands are present near 1620 and 1420 cm^{-1}, probably due to residual species of the precursors, i.e., ammonia and ammonium ions.

Furthermore, a weak component is observed in the spectrum of the support at 2014 cm^{-1} (Fig. 5a), closely corresponding with the positions of a band detected on “binary” WO_3/TiO_2 catalyst, due to the first overtone of the W=O stretching mode surface wolframyl species [6]. This absorption appears more intense for both the fresh and used catalysts, and a shoulder is observed at 2048 cm^{-1}. This last component could be due to the first overtone of the V=O stretching mode of surface vanadyl groups [16]. The observed frequencies, 2048 and 2014 cm^{-1}, due to 2νV=O and 2νW=O, respectively, are very similar to those observed for “binary” V_2O_5/TiO_2 [16] and WO_3/TiO_2 [6] catalysts. This indicates that such vanadyl and wolframyl species, although very sensitive to contaminants and adsorbed molecules (see below), are unperturbed on the catalyst by the presence of other oxo-ions (wolframyl or vanadyl, respectively, and sulphate species, see above).

Finally, all samples exhibit complex features in the 3700–3500 cm^{-1} OH stretching region, besides the 3745 cm^{-1} peak due to silanol groups. In the case of the support (Fig. 5a), these features should be ascribed to hydroxyl groups on the titania surface and to OH species bound to supported tungsten, while for the fresh and used catalysts (Fig. 5b and c) they correspond to those reported for V–W–Ti catalysts [17].

3.4. FTIR studies of adsorbed probe molecules

3.4.1. CO adsorption at 77 K

The adsorption of carbon monoxide was investigated over the bare support and the fresh and used catalyst by the I-2 group. In all cases the samples were outgassed and re-oxidised at 623 K prior CO adsorption. The spectra of CO adsorbed at 77 K on the WO_3/TiO_2 support are reported in Fig. 6A. At high CO coverage (Fig. 6A, a) two peaks at 2190 and 2165 cm^{-1} are observed. The first band can be assigned to CO molecules stabilised on surface coordinatively unsaturated (cus) Ti^{4+} ions [18–22], while the second component could be due to CO molecules hydrogen bonded to surface –OH Brønsted sites, as recently reported for a WO_3/ZrO_2 catalyst [23]. At lower frequency, a broad and complex shoulder in the 2150–2140 cm^{-1} range is also present, their components being assignable to CO adsorbed on surface –OH groups (near 2150 cm^{-1}) [22] and to liquid-like carbon monoxide in micropores (near 2140 cm^{-1}) [4]. By decreasing the CO coverage, this last component is the first to disappear, as CO in

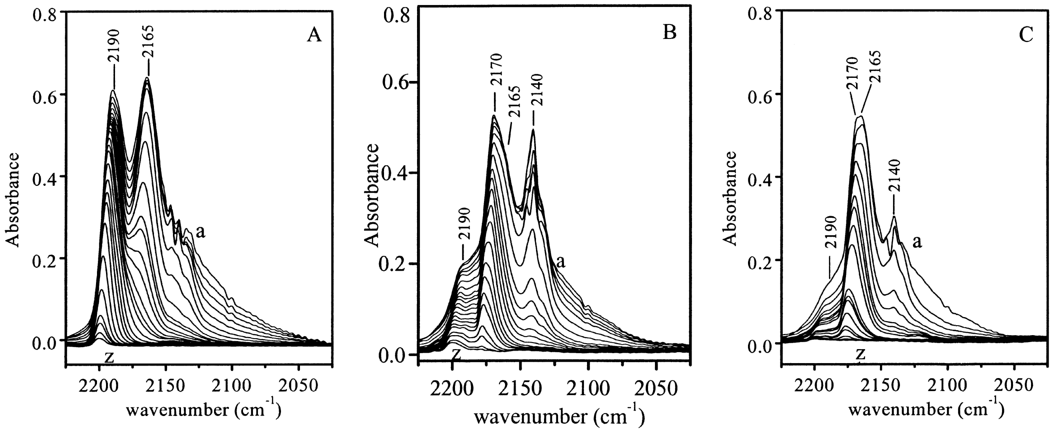

Fig. 6. FTIR spectra of CO adsorbed at 77 K on the TiO_2 support (section A) and on the fresh (section B) and used (section C) EUROCAT SCR catalyst outgassed at 623 K for 1 h and re-oxidised at the same temperature (see Section 2). Curves in the three sections are progressively decreasing CO coverages from (a) the presence of 100 Torr CO to (z) after outgassing for 5 min at 77 K (Laboratory I-2).

liquid-like form and CO adsorbed on hydroxyls are very weakly held on the surface, followed by the 2165 and the 2190 cm^{-1} bands in the order, as CO adducts on Brønsted –OH groups (band at 2165 cm^{-1}) are less stable than those on highly energetic (cus) Ti^{4+} Lewis acid centres (band at 2190 cm^{-1}, Fig. 6A, a–z).

In the case of the fresh catalyst (Fig. 6B) the spectra at high CO coverage are dominated by two main peaks at 2170 and 2140 cm^{-1}, this last being significantly more intense than for the bare support, while the 2190 cm^{-1} component is strongly reduced in intensity, appearing as a partly resolved shoulder. This last feature clearly indicates that Ti^{4+} cations on the surface of the catalyst are largely covered by the supported phase, as they are not accessible to CO. The increase in intensity of the 2140 cm^{-1} band suggests that a larger amount of CO is present into the pores of the catalyst in form of a liquid-like phase. This behaviour could be ascribed to an increase of the covalent character of the catalyst surface due to the presence of the supported phase. The peak at 2170 cm^{-1} appears as a peculiar feature of the catalyst, and could be due to CO adsorbed on Brønsted –OH groups perturbed by the supported species. These sites exhibit a slightly stronger Brønsted character than the sites responsible of the CO stretching band at 2165 cm^{-1}, observed in this case as a shoulder.

On the used catalyst the 2190 cm^{-1} component appears weaker in intensity than on the fresh one, indicating that a further decrease of the number of Ti^{4+} exposed on the surface of the WO_3/TiO_2 support occurred during the operation on stream in the industrial power plant (Fig. 6C). This could be associated with the contamination of the catalyst by some poisons. A slight decrease in intensity of the 2170 cm^{-1} band with respect to the 2165 cm^{-1} component is also observed. Furthermore, the 2140 cm^{-1} component appears less intense than for the fresh catalyst, suggesting some changes in the porous texture of the catalyst occurred during the catalytic run.

3.4.2. NH_3 *adsorption*

The FTIR spectra of adsorbed ammonia have been recorded by the laboratories F-1 and I-1. The results show that ammonia adsorption gives rise to both molecular species coordinated on Lewis acid sites and ammonium ions formed on Brønsted sites.

The IR spectra recorded by the group I-1 of the fresh catalyst (Fig. 7) after contact with NH_3 show the bands of ammonia adsorbed molecularly on Lewis acid sites at 1608 cm^{-1} ($\delta_{as}NH_3$) and the corresponding N–H stretching at 3410, 3385, 3280 and 3180 cm^{-1}, and on Brønsted acid sites at 1667 ($\delta_{as}NH_4$) and 1462 cm^{-1} ($\delta_{as}NH_4$) and the associated stretches in the 3100–2600 cm^{-1} region. The bands associated with ammonium ions decrease in intensity by outgassing at increasing temperature and com-

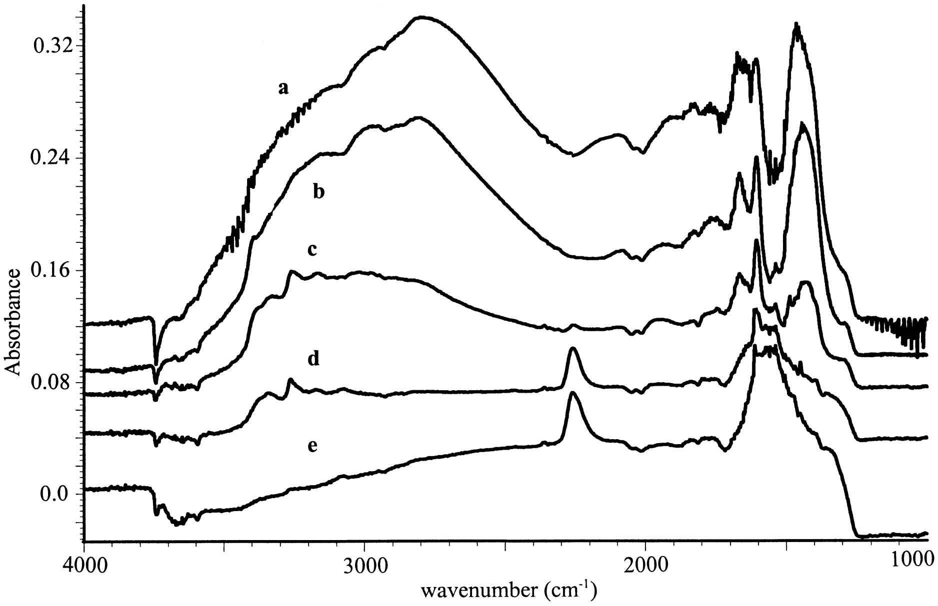

Fig. 7. FTIR spectra of ammonia adsorbed on the fresh EUROCAT SCR catalyst in contact with the gas (a) and after outgassing at room temperature (b), 423 K (c), 523 K (d) and 623 K (e). The spectra are reported in absorbance, having subtracted the spectrum of the catalyst before NH_3 as background (Laboratory I-1).

pletely disappear after evacuation at 523 K (Fig. 7d), while the bands associated with ammonia on Lewis acid sites are, although strongly reduced in intensity, still detectable after outgassing at 623 K (Fig. 7e). On the other hand, in the used sample, the bands associated with coordinated ammonia also completely disappeared in the spectrum recorded after evacuation at 523 K (spectrum not reported for the sake of brevity). This indicates that the Lewis acidity of the used sample is weaker than that of fresh sample. This could be associated with contamination of the catalyst by basic poisons, like alkali or alkaline-earth cations. It must be noticed that the presence of some poisons on the used catalyst was also suggested by the spectral features of adsorbed CO.

After evacuation at 423 and 523 K, two additional very weak bands at 1489 and 1450 cm^{-1} are detectable on the fresh catalyst (Fig. 7b and c). Both these bands completely disappear on increasing the temperature of evacuation from 523 to 623 K (Fig. 7d). These bands, previously observed on other catalytic systems based on different transition metals supported on titania, active both in SCR and in SCO reactions [24], are typical products of ammonia oxidation and have been tentatively assigned to adsorbed nitroxyl HNO and NH species, respectively. These species can be intermediate in the catalytic oxidation of ammonia and are both involved in competitive reactions with respect to SCR. After evacuation at room temperature a very weak band at 1540 cm^{-1} is also detected. As discussed elsewhere [25] this band can be assigned to amine NH_2 species, an activated form of ammonia, and can be intermediate in SCR reaction.

In the subtraction spectra “negative” bands (i.e., bands due to species that are present at the surface of the catalyst before the adsorption of ammonia and that are perturbed or destroyed after the contact) are observed at 2048 and 2014 cm^{-1}. These bands correspond to the first overtone of the V=O or W=O vibration, respectively (see above), which are perturbed by the coordination of ammonia to V^{5+} and W^{6+} ions in surface vanadyl and wolframyl.

After evacuation at 523 K a quite intense new band at 2256 cm^{-1} was detected. This band could be assigned to a surface species produced by reaction of oxidation of ammonia with traces of hydrocarbon present

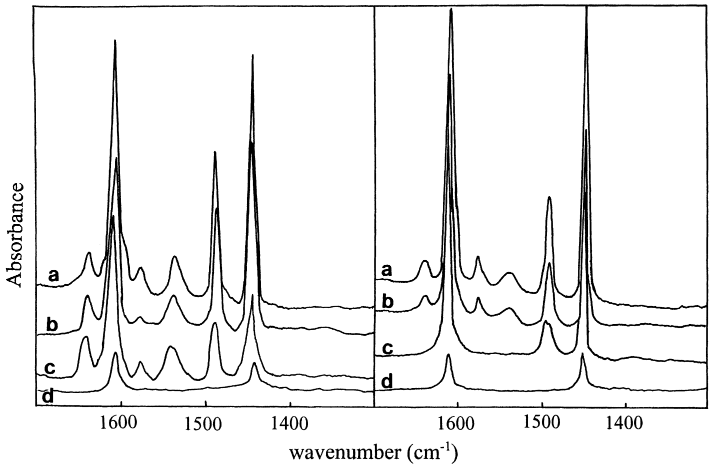

Fig. 8. FTIR spectra of pyridine adsorbed on the fresh (section A) and used (section B) EUROCAT SCR catalysts pre-outgassed at 673 K for 2 h. Samples were contacted at room temperature with pyridine vapour and then outgassed at room temperature (a), 373 K (b), 473 K (c) and 573 K (d) (Laboratory E-2).

at the surface of the catalyst, as indicated by the weak bands in the 3100–2800 cm^{-1} region observable in the spectra of Fig. 5.

3.4.3. Pyridine adsorption

The FTIR spectra of adsorbed pyridine have been recorded by the D-1, E-2 and F-1 laboratories. All these groups found that the adsorption of pyridine gives rise to both molecular species coordinated to Lewis acid sites and pyridinium ions formed on Brønsted sites. As shown in Fig. 8, reporting the spectra obtained by the E-2 group, the bands at 1608, 1580 and 1448 cm^{-1} are due to pyridine adsorbed on Lewis acid centres [26], that resist outgassing at 573 K (Fig. 8A, b). The bands at 1639, 1540 and 1488 cm^{-1} characterised the presence of pyridinium ions [27], which disappeared by outgassing at 573 K (Fig. 8A, b). The spectra recorded with the used sample are apparently similar (Fig. 8B), although the intensity ratio between the bands of Brønsted bonded pyridine with respect to the Lewis bonded one is slightly more favourable to these last species.

3.4.4. $B(OCH_3)_3$ adsorption

The presence of nucleophilic centres on the surface of both the fresh and used catalysts was investigated by the E-2 group by recording the infrared spectra of adsorbed boric acid trimethyl ester. In the case of the fresh catalysts the adsorption of $B(OCH_3)_3$ produced only very weak bands in the 1500–1300 cm^{-1} range (spectra not shown for the sake of brevity), while for the used catalyst two peaks at 1488 and 1363 cm^{-1} were observed, the second component exhibiting a shoulder at 1392 cm^{-1} (Fig. 9a). The

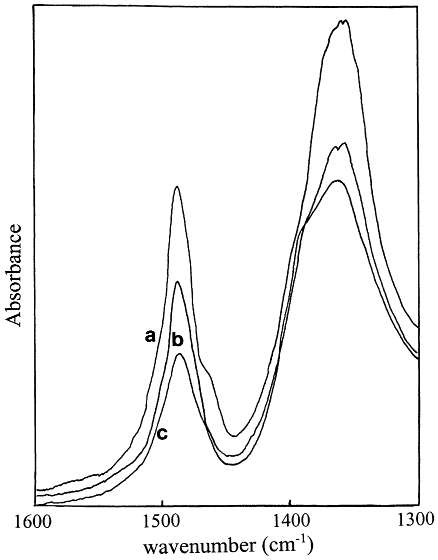

Fig. 9. FTIR spectra of $B(OCH_3)_3$ adsorbed on the used EUROCAT SCR catalyst. Sample was contacted at room temperature with $B(OCH_3)_3$ vapour and then outgassed at room temperature. (a), 373 K (b) and 473 K (c) (Laboratory E-2).

band at 1488 cm^{-1} should correspond to the symmetric $–CH_3$ deformation mode, while absorptions in the 1400–1300 cm^{-1} range should be due to B–O stretching. This mode was found to be sensitive to the basic strength of the adsorbing centres, its location being shifted to higher frequency as the basic strength of the adsorbing sites increases [28]. The two components at 1392 and 1363 cm^{-1} may then originate by the presence of two types of surface sites with different Lewis basic strength (probably, oxygen anions in different coordination environment or different electron density). By outgassing at increasing temperature all spectral components decrease in intensity, but the 1392 cm^{-1} one exhibits a higher resistance to desorption, becoming progressively better defined (Fig. 9b and c). This behaviour confirms that the adsorbed species responsible for this higher frequency component are stabilised on more Lewis basic sites.

These results indicate that essentially no basic sites are present on the fresh catalyst, whereas nucleophilic centres are produced on its surface during the catalytic run.

3.4.5. *Study of the NH_3–NO interaction*

Laboratory F-1 performed experiments on the adsorption of NO and ammonia and on their coadsorption. NO alone adsorbs weakly on the catalyst surface, if at all. No bands of adsorbed nitric oxide as such could be detected, in agreement with previous data [25]. As already shown, ammonia is adsorbed both in molecular form and in a protonated form on the catalyst. These authors also found, again in agreement with previous data [25] that ammonia displaces water from the Lewis acid sites. The coadsorption of NO and NH_3 in a 1:1 molar ratio gave rise to the formation of gaseous N_2O (note that gaseous N_2 is undetectable by IR). The spectra of the surface species formed upon contact with the NO–NH_3 mixture exhibit the absorptions characteristic of coordinated and protonated ammonia, and bands due to newly formed molecular water adsorbed on the catalyst surface are observed in addition. Unfortunately, owing to the IR cut-off limit near 1250 cm^{-1}, it was impossible to analyse in detail the region below 1300 cm^{-1}, where the strong symmetric deformation bands of coordinated ammonia fall. These bands have been found to be the only one allowing the analysis of the behaviour of coordinated ammonia without superimposition with bands of adsorbed water. Apparently, the authors did not obtain evidence on whether the active ammonia species are ammonium ions (as claimed by Topsøe et al. [29,30]) or coordinated ammonia (as proposed by Lietti et al. [31]).

4. Conclusions

The results obtained by vibrational and electronic spectroscopy studies lead to some conclusions about the nature and structure of the surface species in the V_2O_5–WO_3/TiO_2 EUROCAT SCR catalyst.

The V_2O_5 phase covers a large fraction of the WO/TiO_2 support, which contains sulphate impurities. Vanadium is present in the supported phase as pseudo-tetrahedral vanadyl species and in agglomerated structures such as two-dimensional layers and three-dimensional V_2O_5-like species. Similarly, both wolframyl species and WO_3-like structures were detected.

Apparently, vanadyl species are unperturbed by the presence of the wolframyl groups and vice versa. This suggests that no significant interactions between these surface species occur.

Both V^{5+} and W^{6+} ions in V=O and W=O species on the surface act as Lewis acid sites towards ammonia molecules. Furthermore, the formation of ammonium ions by NH_3 adsorption indicated that Brønsted acid sites are also present. Both types of acid site were detected by pyridine adsorption also.

The adsorption of nitric oxide alone and its coadsorption with ammonia indicated that NO molecules interact only weakly with the catalyst surface, while their reduction easily occurs in the presence of NH_3. Unfortunately, no clear evidence on whether coordinated or protonated ammonia molecules are the active species in such process was obtained.

Only minor differences between the surface features of the fresh and used catalyst were observed. In particular, the use of the catalyst in an industrial stream resulted in a slight decrease in the strength of the Lewis acid sites and the appearance of some nucleophilic centre. This behaviour suggests that a limited poisoning of the catalyst by deposition of basic species occurred.

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