

FTIR study of low-temperature CO adsorption on pure Al₂O₃-TiO₂ and V/Al₂O₃-TiO₂ catalysts

P. Concepción,^a B. M. Reddy,^{ab} and H. Knözinger^a

^a *Institut für Physikalische Chemie, Universität München, Büttenandtstrasse 5-13, Haus E, 81377 München, Germany*

^b *Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad-500 007, India*

Received 5th March 1999, Accepted 19th April 1999

Adsorption of CO at low temperature (77 K) on Al₂O₃-TiO₂ and V₂O₅(12 wt.%) / Al₂O₃-TiO₂ samples was studied by FTIR spectroscopy. IR spectroscopy of CO adsorbed at low temperature on Al₂O₃-TiO₂ samples suggests an enrichment of TiO₂ on the catalyst surface. The IR spectra of the calcined (at 773 K) V₂O₅(12 wt.%) / Al₂O₃-TiO₂ sample exhibits two kinds of vanadium species, monomeric tetrahedral V⁵⁺ = O species (band at 1035 cm⁻¹) and an amorphous VO_x monolayer phase (band at 1002 cm⁻¹). CO adsorption at low temperature on this sample shows the presence of V⁴⁺ ← CO carbonyl species (band at 2197 cm⁻¹). As reported in the literature no V⁵⁺ carbonyl species are observed. Reduction of the V₂O₅(12 wt.%) / Al₂O₃-TiO₂ sample at 773 K induces a rearrangement of the amorphous VO_x phase, as indicated by the disappearance of the band at 1002 cm⁻¹. Reduced vanadium species, mainly V³⁺ species, were observed by CO adsorption at low temperature. This V³⁺ ← CO carbonyl complex (monitored by a band at 2185 cm⁻¹) is highly resistant to evacuation which suggests some π-back donation. The V³⁺ species are highly stable towards reoxidation at low temperature. Reoxidation at room temperature leads to a restoration of the V⁵⁺ and V⁴⁺ species as observed in the oxidized samples. Only a small amount of V³⁺ species can not be completely oxidized remaining in an oxidation state of 4+. Hence, two bands at 2197 and 2194 cm⁻¹ were observed and assigned to two different V⁴⁺ Lewis acid sites.

Introduction

Supported vanadium oxide catalysts have been studied quite extensively¹⁻³ because of their technological importance in several industrial heterogeneous catalytic processes, such as partial oxidation of *o*-xylene,^{4,5} ammoxidation of aromatic compounds,^{6,7} and selective catalytic reduction (SCR) of nitrogen oxides.⁸ A large number of experimental techniques have been applied by different research groups in order to elucidate the structure of the surface species and their catalytic properties. However, it is still not possible to give a definitive description of the surface structure and its relation to the catalytic properties of the vanadium oxide surface species.

Among various supported vanadium oxide catalysts the V₂O₅/TiO₂ combination has attracted much attention because of its high selectivity in selective oxidations and its high activity for the SCR of NO_x with NH₃. The SCR of NO_x with NH₃ is mainly employed to reduce atmospheric pollution from stationary power plants and chemicals production establishments, and this process has gained tremendous importance recently due to the ever more stringent emission regulations in many countries. Therefore, several studies were directed towards the development of new types of catalysts that satisfy the needs of practical applications and to the characterization of the nature of SCR catalysts and the elucidation of the structure of the active phase of the catalysts by different physicochemical techniques. A major disadvantage associated with the TiO₂ support in V₂O₅/TiO₂ catalysts is its relatively low specific surface area and low thermal stability of the active anatase structure at high temperatures. Therefore, titania was combined with alumina or silica, by taking advantage of the

high thermal stability of Al₂O₃ or SiO₂ to stabilize the surface area and the structure of titania. Several studies concerning the structural and catalytic properties of TiO₂-SiO₂ (ref. 9-15) or TiO₂-Al₂O₃ (ref. 16-22) binary oxides have been reported.

The aim of the present study was to follow the structure evolution and redox behaviour of the vanadium oxide phase on the Al₂O₃-TiO₂ binary oxide support by low temperature FTIR spectroscopy of adsorbed CO. Carbon monoxide is one of the best probe molecules for sensitive determination of the nature and strength of aprotic acid sites. Surprisingly, there are only a few studies available on CO adsorption on vanadium-containing samples.²³⁻³³ It is generally accepted that V⁵⁺ ions do not form stable complexes with CO even at low temperature because of their high coordinative saturation and the covalent character of the V-O bond.²⁴⁻²⁶ Some authors^{24,25,27,28} proposed that V⁴⁺(d¹) ← CO carbonyls absorb in the range 2212-2180 cm⁻¹. Alternatively, a number of authors^{25,28-32} have attributed the absorption region of 2190-2178 cm⁻¹ to V³⁺ ← CO carbonyls. These species are difficult to eliminate by evacuation³² which indicates some participation of π-back bonding in the V³⁺(d²) ← CO bond.

Experimental

Catalyst preparation

The Al₂O₃-TiO₂ binary oxide (1 : 1.3 mole ratio) support was prepared by a homogeneous coprecipitation method using urea as the precipitation reagent.²¹ For precipitation with urea, a mixed aqueous solution of TiCl₄ (Fluka, AR grade),

NaAlO₂ (Loba Chemie, GR grade) and urea (Loba Chemie, GR grade) was heated to 368 K while stirring vigorously. To prepare the above mixed aqueous solution, TiCl₄ was first digested in cold concentrated HCl and subsequently diluted with deionized water and then NaAlO₂, dissolved separately in deionized water, was added (pH 2). In about 6 h of heating, as decomposition of urea progressed to a certain extent, the formation of precipitate gradually occurred and the pH of the solution increased to 7–8. The precipitate was aged by heating at 368 K for 6 h more to facilitate aging. The thus obtained coprecipitate was then filtered off, washed several times with deionized water until no chloride ions were detected by addition of AgNO₃, and then dried at 383 K for 16 h. In order to remove residual sodium ions the oven-dried precipitates were again washed several times with ammonium nitrate solution (5%) and dried again at 383 K for 16 h. The oven-dried material was finally calcined at 773 K for 6 h in an open-air furnace.

The V₂O₅/Al₂O₃-TiO₂ catalyst, containing 12 wt.% V₂O₅ was prepared by a standard wet impregnation method. To yield supported vanadia, the required quantity of ammonium metavanadate (Fluka, AR grade) was dissolved in 1 M oxalic acid, and the finely powdered calcined Al₂O₃-TiO₂ support was added to this solution. The excess water was evaporated on a water bath with continuous stirring. The resulting impregnated sample was then dried at 383 K for 12 h and calcined at 773 K for 5 h in a closed electrical furnace in a flowing oxygen atmosphere.

Catalyst characterization

X-ray powder diffraction patterns have been recorded on a Philips PW 1051 instrument, using monochromatized Fe-K α radiation and standard recording conditions. XRD phases present in the samples were identified using the ASTM powder data files. The BET surface areas of the samples were determined on a conventional standard static volumetric high vacuum (1×10^{-4} Pa) system by N₂ physisorption at liquid N₂ temperature and by taking 0.162 nm² as the molecular area of N₂. Before the measurements, the samples were dried *in situ* at 473 K for 2 h under vacuum. The XPS measurements were made on a VG-ESCALAB 210 spectrometer working in the fixed analyzer transmission (FAT) mode with a pass energy of 50 eV and Mg-K α radiation as the excitation source. The binding energies (BE) were referenced to the Ti 2p_{3/2} peak of Ti⁴⁺ at 458.5 eV.³⁴

IR spectroscopic studies were carried out with a Bruker IFS-66 FT-spectrometer at a spectral resolution of 1 cm⁻¹ and collecting 128 scans. Self supporting wafers (*ca.* 10 mg cm⁻²) were prepared from the sample powders and heated directly in the IR cell. Prior to the measurements all samples were activated for 1 h in a flow of oxygen at 773 K followed by 1 h evacuation (10^{-3} Pa) at the same temperature. Reduction of the samples was carried out for 1 h in a flow of hydrogen at 773 K followed by evacuation (10^{-3} Pa) at the same temperature for another hour. A specially constructed cell allowed the IR measurements to be performed at temperatures between 85 K and room temperature (rt).³⁵

Results and discussion

The calcined (773 K) Al₂O₃-TiO₂ support had a BET surface area of 159 m² g⁻¹. The quantity of V₂O₅ required to cover this support surface with a single monolayer can be estimated from the area occupied per VO_{2.5} (10.3×10^4 pm²) unit of V₂O₅.³⁶ However, the experimentally observed maximum amount of V₂O₅ that can be formed as a two-dimensional monolayer on many support oxides was found to depend not only on the support surface areas but also on the concentra-

tion of reactive surface hydroxy groups.² Hence, the monolayer capacity of V₂O₅ was always less than the theoretical estimation and ranged from 0.1 to 0.07 wt.% m⁻² of support surface. Therefore, in the present investigation 12 wt.% of V₂O₅ (corresponding to 0.075 wt.% m⁻²) was impregnated on the Al₂O₃-TiO₂ support. The BET surface of the calcined 12 wt.% V₂O₅/Al₂O₃-TiO₂ catalyst was 122 m² g⁻¹. The decrease in the surface area of Al₂O₃-TiO₂ from 159 to 122 m² g⁻¹ after impregnating with V₂O₅ is probably due to the penetration of dispersed vanadia into the micropores of the support. The XRD measurements revealed that the Al₂O₃-TiO₂ support calcined at 773 K was in an amorphous state with broad background diffraction lines due to a poorly crystallized TiO₂ anatase phase. Further, the Al₂O₃-TiO₂ support was found to be thermally stable even up to 1073 K calcination temperature.²¹ Only the intensity of the TiO₂ anatase lines was increased and became sharper with increase in temperature when this sample was subjected to thermal treatments from 773 to 1073 K.²¹ No characteristic XRD lines of a crystalline V₂O₅ phase were detected in the case of 12 wt.% V₂O₅/Al₂O₃-TiO₂ catalyst. This observation reveals that the vanadia is in a dispersed and amorphous state on the support surface or that the size of microcrystallites is below the detection limits of the XRD technique (<5 nm). The XPS atomic intensity ratio measurements (Ti : Al) showed that the Al₂O₃-TiO₂ support, calcined at 773 K, is enriched in TiO₂ on the surface. This is primarily due to a slight excess of TiO₂ in the Al₂O₃-TiO₂ binary oxide support. In the case of the 12 wt.% V₂O₅/Al₂O₃-TiO₂ catalyst, calcined at the same temperature, the V : Ti intensity ratio was found to be almost equal to the V : Al one indicating a uniform distribution of vanadia on this binary oxide support.³⁷ The binding energy of V 2p_{3/2} was found to be 516.8 eV, indicating the presence of V⁴⁺, and increases to 517.5 when this sample was subjected to 1073 K calcination because of the oxidation of V⁴⁺ to V⁵⁺.³⁷

IR spectroscopy of Al₂O₃-TiO₂

The IR spectrum of the activated binary oxide support (calcined at 773 K in O₂) exhibited a complex spectrum containing a set of low-intensity bands in the $\nu(\text{OH})$ region. Three main bands were observed at 3770, 3724 and 3684 cm⁻¹. They characterise OH stretching modes of different types of surface hydroxy groups. It should be noted that low signal/noise ratio can be achieved in the $\nu(\text{OH})$ region because of the low transmittance of the wafers in this spectral regime. Therefore, exact frequency shifts induced by CO adsorption cannot be determined, although the characteristic effects of H-bonding on the O-H band are clearly detectable. In the low frequency region one band is observed at 965 cm⁻¹ (see Fig. 1, spectrum a). We must indicate that this band was not observed when the spectra were recorded by the KBr technique.²¹ Otherwise this band is shifted by CO adsorption, and is absent in the Al₂O₃-TiO₂ sample after impregnation with vanadium (V₂O₅/Al₂O₃-TiO₂) (see Fig. 1, spectrum b). According to these facts this band cannot be attributed to lattice vibrations of the Al₂O₃-TiO₂ support. Therefore assignment to surface vibrational modes is inferred. Indeed, this kind of surface vibration has already been observed by Morterra and Magnacca³⁸ on alumina samples and by Hadjiivanov *et al.*³⁹ on TiO₂ (anatase) samples.

The spectra of different amounts (equilibrium pressure 1–0.01 kPa) of adsorbed CO at low temperature on the activated sample, and after evacuation under dynamic vacuum (10^{-3} Pa) for increasing periods of time, are presented in Fig. 2. The introduction of small amounts of CO leads to the appearance of two bands in the CO-stretching region with maxima at 2208 and 2190 cm⁻¹. A gradual increase of the adsorbed amounts of CO resulted in a broadening and a weak intensity increase of the higher frequency band and a shift of

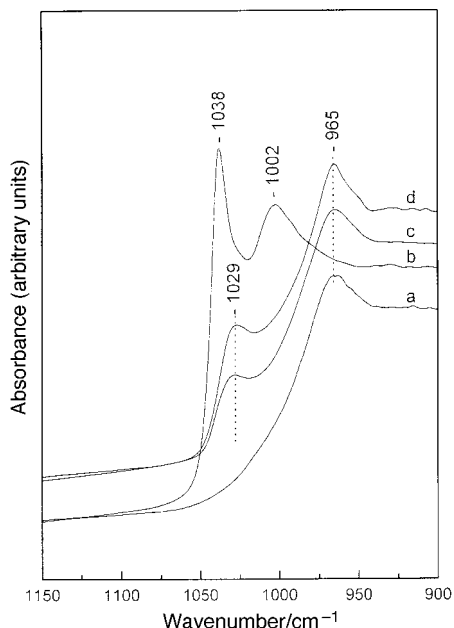


Fig. 1 FTIR spectra in the low frequency region of (a) calcined $\text{Al}_2\text{O}_3\text{-TiO}_2$; (b) calcined $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$; (c) reduced $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ and (d) $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ reoxidized at room temperature.

its maximum to lower frequencies, namely to 2206 cm^{-1} . In contrast to this band, the intensity of that at 2190 cm^{-1} continued to increase and shifted to lower frequencies, namely to 2179 cm^{-1} . New bands were also observed at 2165 , 2156 and 2140 cm^{-1} . The latter band is assigned to physically adsorbed CO and vanished completely after short evacuation. The intensity change of the band at 2156 cm^{-1} occurred simultaneously with a shift of the bands characterizing surface hydroxy groups, and can thus be assigned to CO adsorbed on OH groups. The frequency shift of the OH bands can be estimated to be *ca.* 125 cm^{-1} . The bands at 2206 and 2179 cm^{-1} were highly resistant to evacuation at low temperature and their intensity slowly decreased under dynamic vacuum up to 183 K for the band at lower frequency (2179 cm^{-1} shifted to 2190 cm^{-1}) and up to 233 K for the higher frequency band (2206 cm^{-1} shifted to 2208 cm^{-1}). Adsorption of 5 kPa of CO at room temperature on the same sample led to the appearance of only two bands at 2208 and 2190 cm^{-1} .

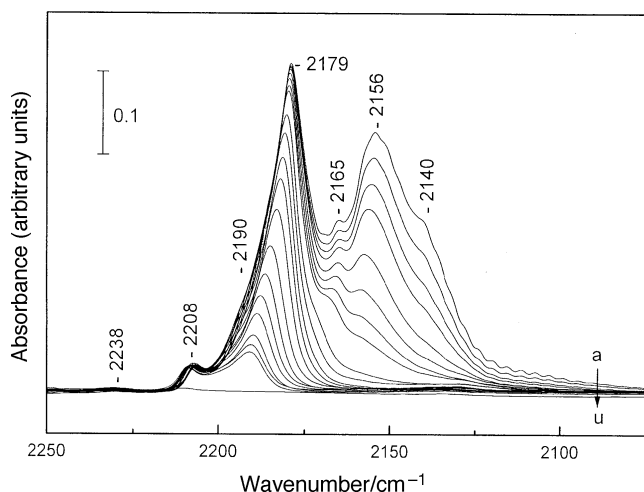


Fig. 2 FTIR spectra of CO ($1\text{--}0.01\text{ kPa}$ equilibrium pressure) adsorbed at 77 K on calcined $\text{Al}_2\text{O}_3\text{-TiO}_2$ and after evacuation in dynamic vacuum (10^{-3} Pa) for increasing time.

It must be pointed out that the overall behaviour of the spectra and the stability of the bands after long evacuation and with increasing temperature is similar to that observed for TiO_2 anatase samples.⁴⁰ Consequently, the bands at higher frequencies (2206 , 2179 and 2165 cm^{-1}) can be assigned to CO coordinated to Ti^{4+} Lewis acid sites having differing acid strength. Only one additional very weak band highly resistant to evacuation was observed at *ca.* 2238 cm^{-1} . It can probably be attributed to surface defects with strong Lewis acid character. The above results seem to indicate a coverage of the Al_2O_3 by TiO_2 . This is in agreement with the XPS results which indicated an enrichment of Ti on the catalyst surface.³⁷

Reduction of the $\text{Al}_2\text{O}_3\text{-TiO}_2$ sample in a flow of H_2 at 773 K for 1 h , led to similar IR spectra as for the calcined sample, also after addition of CO at low temperature. Only one new band appearing at 2199 cm^{-1} as a broad shoulder was observed after addition of small amounts of CO at low temperature (see Fig. 3). This band remained stable even after reoxidation of the reduced sample at room temperature (2 kPa O_2 , 20 min). The assignment of this band is not clear at present. One possibility is to attribute this band to the formation of Ti^{3+} ions after reduction. However, there are many discrepancies in the literature about the $\text{Ti}^{3+} \leftarrow \text{CO}$ band. Some authors attributed a band at 2115 cm^{-1} to CO adsorbed on Ti^{3+} ions.^{41,42} We did not observe a carbonyl band around 2115 cm^{-1} . Other authors attributed the lack of this band to an oxidation of the reduced sample after the introduction of small amounts of CO. They assumed that CO is dissociated, the carbon atom being localized on the supported metal, while the oxygen atom oxidizes the Ti^{3+} ions.⁴⁰ However, it cannot be excluded that the presence of Al^{3+} stabilized some Ti^{3+} ions in the structure. Temperature programmed reduction (TPR) results of the $\text{Al}_2\text{O}_3\text{-TiO}_2$ sample indicated a small reduction of the structure at *ca.* 723 K .³⁷ Another possible assignment of the band observed at 2199 cm^{-1} could be to new Lewis acid sites due to a slight dehydroxylation of the surface or to the formation of small amounts of rutile after reduction. Results from the literature indicate the appearance of only one band at 2193 cm^{-1} after introduction of small amounts of CO on TiO_2 rutile samples.⁴³ It is also possible to attribute this band to Al^{3+}

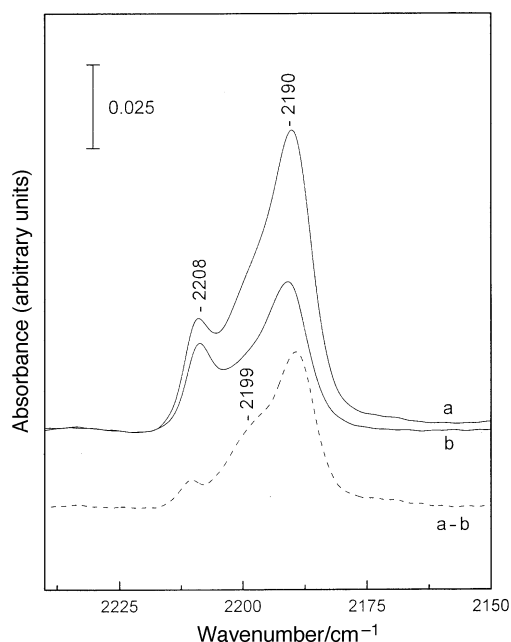


Fig. 3 FTIR spectra of CO adsorbed at 77 K on $\text{Al}_2\text{O}_3\text{-TiO}_2$ (a) calcined at 773 K and (b) reduced at 773 K . The spectra are taken after short evacuation of CO.

Lewis acid sites,^{44,45} which become accessible to CO molecules after reduction of the binary $\text{Al}_2\text{O}_3\text{-TiO}_2$ oxide support.

IR spectroscopy of $\text{V}/\text{Al}_2\text{O}_3\text{-TiO}_2$

Sample calcined at 773 K. The IR spectra of the $\text{V}/\text{Al}_2\text{O}_3\text{-TiO}_2$ sample exhibited bands with very low intensity, as compared to the pure support, in the $\nu(\text{OH})$ region with a maximum at *ca.* 3707 cm^{-1} . The very low intensity of hydroxy bands indicates an interaction of the vanadium species with the hydroxy groups of the support during impregnation, which is in agreement with the formation of a monolayer of vanadia on the $\text{Al}_2\text{O}_3\text{-TiO}_2$ support. In the low frequency region, two bands at 1037 and 1002 cm^{-1} due to V=O stretching vibrations were observed.^{46–52} The band at 965 cm^{-1} observed on the free support disappeared (Fig. 1, spectrum b). This is in concordance with the assignment of this band to surface vibration modes (as discussed in the previous section), which are modified by vanadia interaction with the surface of the $\text{Al}_2\text{O}_3\text{-TiO}_2$ catalyst. According to the literature the band at 1002 cm^{-1} can be assigned to an amorphous two dimensional VO_x monolayer phase.^{46,47} The higher frequency of the 1037 cm^{-1} band indicates the absence of polymer structures and of a separate V_2O_5 phase (sharp absorption bands expected at 1020 and 824 cm^{-1}).⁴⁸ Data in the literature report a band at 1035 cm^{-1} which was attributed to the V=O stretching frequency for VOCl_3 , where isolated $\text{V}^{5+}=\text{O}$ groups exist and V^{5+} ions are four coordinated.^{49,50}

Introduction of 1 kPa of CO at low temperature resulted in the appearance of three bands with maxima at 2197 , 2167 and 2142 cm^{-1} (Fig. 4A, spectrum a). The latter band is attributed to physically adsorbed CO and vanished completely after short evacuation. The increase in intensity of the band at 2167 cm^{-1} is accompanied by a bathochromic shift of the hydroxy bands. Therefore the band at 2167 cm^{-1} can be ascribed to CO adsorbed on OH groups. The position of this band is at higher frequencies than that in the sample without vanadium, which may indicate a higher acidity of the hydroxy groups of V-containing materials. The frequency shift due to the adsorption of CO on the OH groups can be estimated to be *ca.* 150 cm^{-1} . The assignment of these OH groups to V–OH species is not unequivocal. The stretching mode of isolated V–OH surface hydroxy groups^{53,54} has been reported to be located at 3660 cm^{-1} .

Because of the low transmission in the $\nu(\text{OH})$ region, a detailed analysis is not possible. Otherwise the absence of this band could be attributed to a delocalization of the proton as indicated below.

Evacuation of the sample at low temperature led to the presence of only one band at 2197 cm^{-1} , which is stable under dynamic vacuum until approximately 183 K . The position of this band and its stability with increasing temperature under dynamic vacuum is similar to the band at 2190 cm^{-1} observed in the pure $\text{Al}_2\text{O}_3\text{-TiO}_2$ sample, which was assigned to CO adsorbed on Ti^{4+} ions. CO adsorption on V^{4+} species^{24,25,27,28} is expected to give bands at approximately $2212\text{--}2180\text{ cm}^{-1}$, with similar thermal stability. Therefore it is not possible at present to assign this band to CO adsorbed on either Ti^{4+} or V^{4+} Lewis acid sites. However, XPS results of the calcined $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ sample indicated the presence of V^{4+} species. The bands in the low-frequency region at 1037 and 1002 cm^{-1} were also slightly shifted to lower frequencies after CO adsorption. The frequency shift in both cases is about 2 cm^{-1} . The shift of these bands occurred simultaneously with a shift of the OH bands. A restoration of the spectrum of the unperturbed hydroxy groups led to a restoration of the initial positions of both bands (Fig. 4B and C).

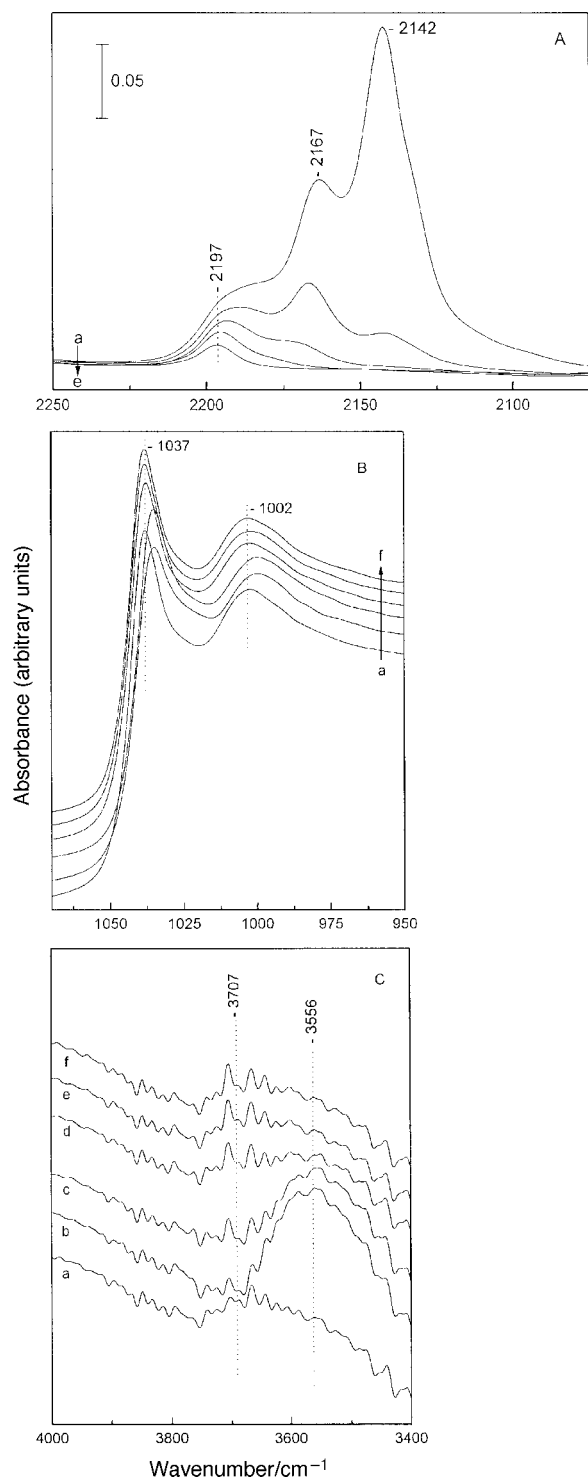
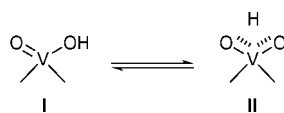


Fig. 4 A. FTIR spectra of CO adsorbed at 77 K on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ calcined at 773 K . Equilibrium pressure of 1 (a) and 0.01 (b) kPa CO and after evacuation of the sample for increasing time (c, d, e). B. FTIR spectra in the low frequency region after CO adsorption at 77 K on calcined $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$. Sample without CO (a), in the presence of CO with equilibrium pressure of 1 (b) and 0.01 (c) kPa CO and after evacuation of the sample for increasing time (d, e, f). C. FTIR spectra in the hydroxy region of calcined $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$. Same notation as in Fig. 4B.

The shift of both bands was independent of CO adsorbed on Lewis acid sites. These results suggest the presence of species like I in Scheme 1. From the above considerations we can infer the existence of two kinds of vanadium species on the calcined $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ catalyst: (i) monomeric vanadium surface species with the following structures (I and II in



Scheme 1

Scheme 1), and (ii) an amorphous two-dimensional VO_x monolayer phase. These species have already been proposed in the literature for vanadium oxide on TiO_2 support.^{55–57}

Samples reduced at 773 K. The IR spectra of the reduced sample showed an increase in the hydroxy band intensity as compared to the calcined sample, with maxima at 3770, 3722 and 3682 cm^{-1} . This observation could be due to the formation of hydroxy groups during the reduction process which are not eliminated during evacuation. In the low frequency region a decrease of the initial band at 1037 cm^{-1} , its maximum being shifted to 1029 cm^{-1} , and a complete disappearance of the band at 1002 cm^{-1} were observed. In contrast, the band at 965 cm^{-1} (observed in the free support) reappeared (Fig. 1, spectrum c). The decrease of the intensity of the band at 1037 cm^{-1} and its shift to lower frequencies could be due to a partial reduction of the V^{5+} species to lower oxidation states and to the formation of V–OH groups at the expense of the V=O bonds. The disappearance of the band at 1002 cm^{-1} indicated a rearrangement of the VO_x amorphous monolayer phase after reduction of the V-containing sample. This could explain the reappearance of the band at 965 cm^{-1} observed also in the free Al_2O_3 – TiO_2 support (Fig. 1, spectrum a). However, this band also can be assigned to surface vanadate species.^{46,47,58}

Addition of 1 kPa of CO at low temperature led to the appearance of three bands in the CO stretching region, namely at 2185, 2158 and 2142 cm^{-1} (Fig. 5). The latter band is attributed to physically adsorbed CO. The intensity change of the band at 2158 cm^{-1} is related to a shift of the OH bands, and can therefore be ascribed to CO adsorbed on hydroxy groups. The position of this band is similar to that observed for the pure Al_2O_3 – TiO_2 system. The band at 2185 cm^{-1} remained unchanged after long evacuation of the sample at low temperature, indicating a strong M–CO bonding. This band is very broad and its intensity remained high even after long evacuation (Fig. 6A, spectrum b). In order to assign this band to vanadium species (with an oxidation state lower than 5+), and to achieve information about its redox behaviour, small amounts of O_2 (1 kPa) were introduced into the IR cell at low temperature for 5 min. After evacuation and adsorption of small amounts of CO at low temperature a new broad

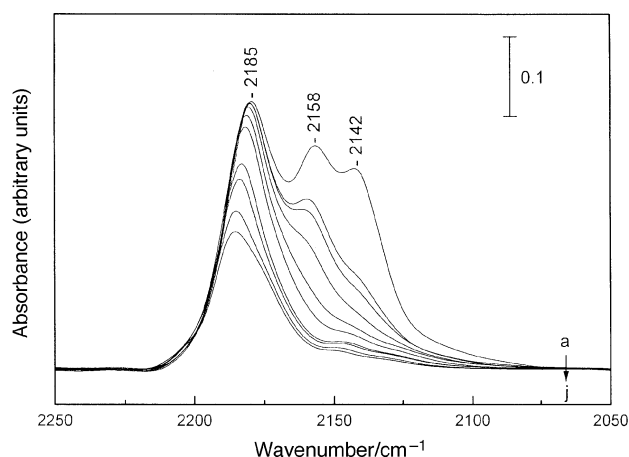


Fig. 5 FTIR spectra of CO adsorbed at 77 K on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ – TiO_2 reduced at 773 K. Equilibrium pressure of 1 (a), 0.05 (b) and 0.03 (c) kPa CO and evacuation of the sample for increasing time (d–g) and under dynamic vacuum (h–j).

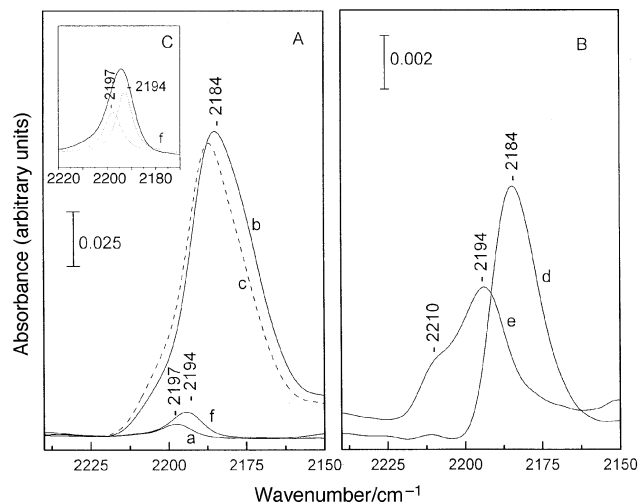


Fig. 6 A. FTIR spectra of CO adsorbed at 77 K on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ – TiO_2 : (a) calcined at 773 K; (b) reduced at 773 K; (c) reoxidized at 77 K (5 min) and (f) reoxidized at room temperature (30 min). The spectra are taken after evacuation of CO. B. FTIR spectra at room temperature of CO adsorbed on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ – TiO_2 : (d) after reoxidation at 77 K and (e) after introduction of 2 kPa O_2 at room temperature. The spectra are taken after evacuation of CO. C. Deconvolution of the spectra (f), after CO adsorption on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ – TiO_2 reoxidized at room temperature.

shoulder at 2209 cm^{-1} was observed, as well as a slight decrease of the band at 2184 cm^{-1} (Fig. 6A, spectrum c). The shoulder observed at 2209 cm^{-1} remained very stable under dynamic vacuum with increasing temperature (up to 273 K), while the band at 2185 cm^{-1} remained stable until room temperature (Fig. 6B, spectrum d). The stability of both bands was higher than that observed for Ti^{4+} ions. We therefore infer that these bands can be attributed to CO adsorbed on V^{n+} species (with $n < 5$). The 2185 cm^{-1} band has lower frequency, but the respective species are more stable than that for the 2209 cm^{-1} band. However, with cations forming predominantly σ -character bonds with CO, the higher stability of the carbonyls corresponds to a higher stretching frequency of the respective band. This implies that both bands (at 2209 and 2185 cm^{-1}) cannot be assigned to carbonyls of vanadium cations having the same oxidation state. The higher stability and the lower frequency of the band at 2185 cm^{-1} as compared to the band at 2209 cm^{-1} suggests some π -back donation. Hence, the band at 2185 cm^{-1} must be attributed to carbonyls formed with the participation of vanadium ions in an oxidation state lower than 4+, and the band at 2209 cm^{-1} to vanadium species with an oxidation state 4+. However, the possibility of some $\text{Ti}^{4+} \leftarrow \text{CO}$ species contributing to the broad band at 2185 cm^{-1} is not excluded. In order to rule out this possibility some additional experiments were performed at room temperature and are discussed below. Another confirmation of the assignment of the bands at 2209 and 2185 cm^{-1} to different oxidation states of the vanadium species is their behaviour after reoxidation in oxygen at room temperature. The spectra of the sample (recorded at rt), before and after introduction of small amounts of oxygen at rt is indicated in Fig. 6B, spectra d and e. Before introduction of O_2 , a band was observed at 2185 cm^{-1} (Fig. 6B, spectrum d). After introduction of 2 kPa of O_2 at rt, the band at 2185 cm^{-1} disappeared and new bands at 2194 and 2209 cm^{-1} were observed (Fig. 6B, spectrum e). According to the redox behaviour, these bands can be attributed to CO bonded to V^{4+} species, and the band at 2185 cm^{-1} to CO bonded to V^{3+} species. After 30 min in an oxygen atmosphere at room temperature, the sample was evacuated and studied again by CO adsorption at low temperature. The results of these experiments are discussed in the following section.

Samples reoxidized at room temperature

The IR spectra of the sample after reoxidation at room temperature showed an increase in the intensity of the band at 1029 cm^{-1} , which agrees with a restoration of the vanadium (V^{5+}) species (species I and II in Scheme 1) by reoxidation of the sample. However, the band at 965 cm^{-1} remained unchanged (Fig. 1, spectrum d) as in the free $\text{Al}_2\text{O}_3\text{-TiO}_2$ support. We therefore infer that this band is more likely due to surface vibration modes rather than to vanadium species.

After introduction of 0.6 kPa of CO at low temperature, two bands were observed in the CO stretching region with maxima at 2185 and 2162 cm^{-1} . The band of physically adsorbed CO is not observed because of the low CO coverage in this experiment. The band at 2162 cm^{-1} can be assigned to CO adsorbed on OH groups. This band was also observed for the calcined sample and was assigned to CO bonded on $V^{5+}\text{-OH}$ species. This is in agreement with a restoration of these species by reoxidation of the sample. Difference spectra showed the presence of another band at 2156 cm^{-1} observed also in the reduced sample and in the pure $\text{Al}_2\text{O}_3\text{-TiO}_2$ support without vanadium. This band can be attributed to CO bonded to hydroxy groups of the support. The band at 2185 cm^{-1} resulted from a shift to lower frequencies of the band at 2194 cm^{-1} as can be also observed from the difference spectra. This band remained stable under dynamic vacuum (Fig. 6A, spectrum f) and at increasing temperature up to 163 K. Deconvolution of the band showed two bands, one at 2197 cm^{-1} , also observed for the calcined sample (Fig. 6A, spectrum a), and a new one with maximum at 2194 cm^{-1} (Fig. 6C). The latter band can be assigned to some V^{4+} species resulting from an incomplete reoxidation of the V^{3+} species. The band at 2209 cm^{-1} observed immediately after introduction of O_2 at room temperature, was not observed because of a consecutive oxidation of the V^{4+} species to V^{5+} during the time of exposure of the sample to O_2 .

As indicated in previous sections the band at 2197 cm^{-1} can be assigned to CO bonded either to V^{4+} or Ti^{4+} Lewis acid sites. The possibility of bands due to Ti^{4+} species being superimposed by the broad 2185 cm^{-1} band in the reduced samples can not be excluded. Therefore experiments of adsorption of CO (5 kPa) at room temperature were performed on the calcined, reduced and reoxidized $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ samples. The band at 2197 cm^{-1} was observed in calcined and reoxidized samples, however, it was not apparent in reduced samples. If the band at 2197 cm^{-1} is attributed to CO coordinated to Ti^{4+} Lewis acid sites, and is observed in the reduced samples after oxidation, it must also be observed in the reduced samples, at least if reorganizations of the structure during reoxidation can be excluded, as in our case. Therefore, we infer that this band is characteristic of a $V^{4+}\text{-CO}$ complex.

Conclusions

$\text{Al}_2\text{O}_3\text{-TiO}_2$ calcined at 773 K is in an amorphous state with a high surface area ($159\text{ m}^2\text{ g}^{-1}$). IR spectroscopy of CO adsorbed at low temperature as well as XPS measurements suggest a coverage of Al_2O_3 by TiO_2 .

The IR spectra of the calcined 12 wt.% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ sample contain bands of two different vanadium species, monomeric tetrahedral $V^{5+}=\text{O}$ species and an amorphous VO_x monolayer phase. According to XPS results V^{4+} species are also present in the calcined sample,³⁷ responsible for the 2197 cm^{-1} band observed after CO adsorption at low temperature. As reported in the literature no V^{5+} carbonyl species are observed.

Reduction of the 12 wt.% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ sample at 773 K leads to the formation of V^{3+} species monitored by a band at 2185 cm^{-1} after CO adsorption at 77 K. The IR spectra

show a rearrangement of the amorphous VO_x phase (disappearance of the band at 1002 cm^{-1}), and reappearance of a band at 965 cm^{-1} due to surface vibration modes of the $\text{Al}_2\text{O}_3\text{-TiO}_2$ support.

The V^{3+} species in the 12 wt.% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ reduced sample are stable towards reoxidation at low temperature (77 K). Reoxidation at room temperature leads to a restoration of the V^{5+} and V^{4+} species observed in the oxidized sample. However, some V^{3+} species are not completely oxidized remaining in an oxidation state of 4+ (band at 2194 cm^{-1}).

The frequencies at which $V^{4+} \leftarrow \text{CO}$ and $\text{Ti}^{4+} \leftarrow \text{CO}$ carbonyls appeared and the stability of these species toward evacuation at low and increasing temperatures are similar. In order to discriminate between both kinds of species, a comparative study of CO adsorption at room temperature on calcined, reduced and reoxidized 12 wt.% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-TiO}_2$ samples was necessary.

Acknowledgements

B.M.R. acknowledges a visiting fellowship from the Deutscher Akademischer Austauschdienst and P.C. for a grant from the Fonds der Chemischen Industrie. We are grateful to Dr K. Hadjiivanov for valuable discussions. The work was financially supported by the Deutsche Forschungsgemeinschaft (SFB 338) and by the Fonds der Chemischen Industrie.

References

- 1 P. J. Gellings, in *Catalysis*, ed. G. C. Bond and G. Webb, The Royal Society of Chemistry, London, 1985, Vol. 7, p. 105.
- 2 G. C. Bond and S. F. Tahir, *Appl. Catal.*, 1991, **71**, 1 and references therein.
- 3 G. Deo, I. E. Wachs and J. Haber, *Crit. Rev. Surf. Chem.*, 1994, **4**, 141.
- 4 M. S. Wainwright and N. R. Foster, *Catal. Rev. Sci. Eng.*, 1979, **19**, 211.
- 5 V. Nikolov, D. Klissurski and A. Anastasov, *Catal. Rev. Sci. Eng.*, 1991, **33**, 1.
- 6 P. Cavelli, F. Cavani, I. Manenti and F. Trifiro, *Catal. Today*, 1987, **1**, 245.
- 7 M. Sanati and A. Andersson, *J. Mol. Catal.*, 1990, **59**, 233.
- 8 H. Bosch and F. Janssen, *Catal. Today*, 1988, **2**, 369.
- 9 R. Castillo, B. Koch, P. Ruiz and B. Delmon, *J. Catal.*, 1996, **161**, 524.
- 10 D. C. M. Dutoit, M. Schneider, R. Hutler and A. Baiker, *J. Catal.*, 1996, **161**, 651.
- 11 Z. Liu and R. J. Davis, *J. Phys. Chem.*, 1994, **98**, 1253.
- 12 S. Imamura, T. Nakai, H. Kanai and T. Ito, *Catal Lett.*, 1994, **28**, 277.
- 13 B. E. Handy, A. Baiker, M. Schraml-Marth and A. Wokaun, *J. Catal.*, 1992, **133**, 1.
- 14 V. M. Ogenko, A. V. Fesenko, N. D. Konovalova and V. I. Stepanenko, *React. Kinet. Catal. Lett.*, 1995, **54**, 355.
- 15 B. M. Reddy, S. Mehdi and E. P. Reddy, *Catal. Lett.*, 1993, **20**, 317.
- 16 E. Rodenas, T. Yamagouchi, H. Hattori and K. Tanabe, *J. Catal.*, 1981, **69**, 434.
- 17 M. A. Stranick, M. Houalla and D. M. Hercules, *J. Catal.*, 1987, **106**, 362.
- 18 Z. Wei, Q. Xin, X. Guo, E. L. Sham, P. Grange and B. Delmon, *Appl. Catal.*, 1990, **63**, 305.
- 19 J. Ramirez, L. Ruiz-Ramirez, L. Cedeno, V. Harle, M. Vrinat and M. Breyse, *Appl. Catal.*, A, 1993, **93**, 163.
- 20 H. M. Matralis, M. Ciardelli, M. Ruwet and P. Grange, *J. Catal.*, 1995, **157**, 368.
- 21 B. M. Reddy, M. V. Kumar, E. P. Reddy and S. Mehdi, *Catal. Lett.*, 1996, **36**, 187.
- 22 A. Gutierrez-Alejandro, M. Gonzalez-Cruz, M. Trombetta, G. Busca and J. Ramirez, *Microporous Mesoporous Mater.*, 1998, **23**, 265.
- 23 A. Davydov, A. Budneva and N. G. Maksimov, *React. Kinet. Catal. Lett.*, 1982, **20**, 93.
- 24 A. Davydov and M. Shepotko, *Teor. Ekspn. Khim.*, 1990, **26**, 505.

- 25 Z. Sobalic, R. Kozlowski and J. Haber, *J. Catal.*, 1991, **127**, 665
- 26 B. Jonson, B. Rebenstorf, R. Larsson and S. L. T. Andersson, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 1897.
- 27 S. Gerasimov and V. Filimonov, *Kinet. Katal.*, 1981, **22**, 469.
- 28 B. Jonson, B. Rebenstorf and R. Larsson, *Acta Chem. Scand.*, 1988, **A42**, 156.
- 29 B. Jonson, B. Rebenstorf, R. Larsson and S. L. T. Andersson, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 3363.
- 30 B. Rebenstorf, M. Berglund, R. Lykvist and R. Larsson, *Z. Phys. Chem. (Munich)*, 1981, **126**, 595.
- 31 A. Maschenko, M. Kou, V. Shvetz and V. Kazanskii, *Teor. Eksp. Khim.*, 1972, **8**, 801.
- 32 G. Busca, G. Ramis and V. Lorenzelli, *J. Mol. Catal.*, 1989, **50**, 231.
- 33 B. Jonson, B. Rebenstorf, R. Larsson, S. L. T. Andersson and S. T. Lundin, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 767.
- 34 B. M. Reddy, B. Chowdhury, I. Ganesh, E. P. Reddy, T. C. Rojas and A. Fernandez, *J. Phys. Chem. B*, 1998, **102**, 10176.
- 35 R. Liu, Doctoral Dissertation, Universität München, 1989.
- 36 F. Roozeboom, M. C. Mittlemeijer-Harzeleger, J. A. Moulijn, J. Medema, V. H. J. de Beer and P. J. Gellings, *J. Phys. Chem.*, 1980, **84**, 2783.
- 37 B. M. Reddy, B. Chowdhury, E. P. Reddy and A. Fernandez, unpublished results.
- 38 C. Morterra and G. Magnacca, *Catal. Today*, 1996, **27**, 497.
- 39 K. Hadjiivanov, O. Saur, J. Lamotte and J. C. Lavalley, *Z. Phys. Chem.*, 1994, **187**, 281.
- 40 K. Hadjiivanov, J. Lamotte and J. C. Lavalley, *Langmuir*, 1997, **13**, 3374.
- 41 L. Yi, G. Ramis, G. Busca and V. Lorenzelli, *J. Mater. Chem.*, 1994, **4**, 175.
- 42 G. Busca, H. Saussey, O. Saur, J. C. Lavalley and V. Lorenzelli, *Appl. Catal.*, 1985, **14**, 245.
- 43 K. Hadjiivanov, *Appl. Surf. Sci.*, 1998, **135**, 331.
- 44 M. I. Zaki, B. Vielhaber and H. Knözinger, *J. Phys. Chem.*, 1986, **90**, 3176.
- 45 C. Morterra, S. Coluccia, E. Garone and G. Ghiotti, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 289.
- 46 A. Sarkany and G. D. Parfitt, *J. Catal.*, 1979, **57**, 476.
- 47 Y. Nakagawa, T. Ono, H. Miyata and Y. Kubokawa, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2929.
- 48 G. C. Bond, A. Sarkany and G. D. Parfitt, *J. Catal.*, 1979, **57**, 476.
- 49 C. G. Barraclough, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3552.
- 50 T. J. Dines, C. H. Rochester and A. M. Ward, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 653.
- 51 J. M. Jehng, G. Deo, B. Weckhuysen and I. E. Wachs, *J. Mol. Catal. A: Chem.*, 1996, **110**, 41.
- 52 I. Georgiadou, Ch. Papadopoulou, H. K. Matrralis, G. A. Voyiatzis, A. Lycourghiotis and Ch. Kordulis, *J. Phys. Chem. B*, 1998, **102**, 8459.
- 53 G. Busca, G. Centi, L. Marchetti and F. Trifiró, *Langmuir*, 1986, **2**, 568.
- 54 G. Busca, G. Centi, L. Marchetti and F. Trifiró, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1003.
- 55 M. M. Kantcheva, K. I. Hadjiivanov and D. G. Klissurski, *J. Catal.*, 1992, **134**, 299.
- 56 G. C. Bond, J. P. Zurita, S. Flamerz, P. J. Gellings, H. Bosch, J. G. Ommen and B. J. Kip, *Appl. Catal.*, 1986, **22**, 361.
- 57 G. C. Bond and S. F. Tahir, *Appl. Catal.*, 1991, **71**, 1.
- 58 G. Hausinger, H. Schmelz and H. Knözinger, *Appl. Catal.*, 1988, **39**, 267.

Paper 9/01776C