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Active sites in vanadia/titania catalysts for selective aerial oxidation of β -picoline to nicotinic acid

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ABSTRACT

Vanadia/titania catalysts with varying vanadium content were prepared by impregnation using three different titania carrier materials of varying surface area. The structure of active vanadium species for β -picoline oxidation was investigated. Vanadium is mainly in the +5 oxidation state as revealed by electron paramagnetic resonance (EPR) and ⁵¹V magic-angle spinning nuclear magnetic resonance (⁵¹V MAS NMR) spectroscopy techniques. Diffuse reflectance UV-visible (DRUV-vis) spectroscopy and spectral deconvolution enabled identification of at least five different types of vanadium oxide species in these catalysts: monomeric tetrahedral VO₄³⁻, polymeric distorted tetrahedral VO₃³⁻, square pyramidal V₂O₅, octahedral V₂O₆²⁻ and V⁴⁺ oxide species. While both VO₄³⁻ and VO₃³⁻ species are active in β -picoline oxidation, the latter having a distorted tetrahedral geometry yielded the desired products—picolinaldehyde and nicotinic acid. High surface area, anatase structure for the support and dispersed, distorted tetrahedral vanadium oxide species are the key parameters determining the activity and selectivity of these oxidation catalysts.

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1. Introduction

Supported vanadium oxides have been extensively investigated as interesting catalytic materials [1-11]. Among them, vanadia/titania have a high commercial potential as oxidation catalysts in several industrial processes including oxidation of o-xylene to phthalic anhydride, butane and pentane to maleic anhydride and alkyl aromatics to the corresponding aldehydes and acids, oxidative dehydrogenation of alkanes to olefins and oxidative destruction of chlorinated hydrocarbons [1-6,12-15]. They are also used in selective catalytic reduction (SCR) of NO_x with NH_3 [16]. Their efficient catalytic activity for the oxidation of β -picoline to nicotinic acid, a pro-vitamin and an important intermediate in the production of pharmaceuticals and food additives, with molecular oxygen was reported by several of us [17]. High selectivity and conversion were achieved. The nature of the TiO₂ carrier had a marked influence on the catalytic activity and selectivity [17]. We report here studies on the structure of active vanadium species in vanadia/titania catalysts for this reaction.

In general, structure and physicochemical properties have a strong effect on the catalytic performance of these catalysts in oxidation reactions [1–6]. The method of preparation, type of

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starting materials, calcination temperature, nature of titania support, additives/impurities and the acid and base properties of the support influence the surface vanadium species and catalytic activity/selectivity. Despite various characterization studies of the vanadia-titania catalysts by different techniques, the type and structure of the surface vanadium species active in oxidation reactions has not been completely understood [18-28]. Different vanadium structures viz., isolated vanadium species (in tetrahedral and octahedral coordination), polymeric-type species (spread over titanium oxide) and bulk vanadium oxide (either in amorphous or crystalline form) have been proposed to be present on the surface in varying amounts. During the oxidation reactions, these structures can undergo conversion from one to the other. Which of these species are active in specific oxidation reactions and how their concentration and reducibility are affected by the reaction conditions and the presence of hydrocarbon substrates are important questions. An understanding of the structure, state and concentration of vanadium species should possibly enable development of more efficient selective oxidation catalysts.

A heterogeneous composition of vanadium species makes the analysis more complex and challenging. However, by using a combination of complementary spectroscopic techniques it should be possible, in principle, to determine the structure of the active vanadium species. In view of this, nine different vanadia/titania catalyst samples have been prepared by impregnation from three differ-

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ent titania support materials with varying amounts of vanadia. The catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption/desorption, temperature-programmed desorption of adsorbed ammonia (NH₃-TPD), ⁵¹V magic-angle spin nuclear magnetic resonance (MAS NMR), diffuse reflectance UV-visible (DRUVvis) and electron paramagnetic resonance (EPR) spectroscopy techniques. Different types of surface vanadium species have been identified and quantified. A correlation between the concentration of different vanadium species and catalytic activity/selectivity enabled determination of the active vanadium species in the oxidation of β -picoline to nicotinic acid.

2. Experimental

2.1. Materials

In the preparation of vanadia/titania catalysts, three different TiO₂ anatase materials-A, B, and C were used as supports. The BET-surface area of A was 300 m^2/g , while B and C had surface areas of around 130 m^2/g . The support material was mixed (for 60 min) with oxalic acid and water in a mass ratio of 71:4:25. The mixtures were extruded (nozzle diameter of the extrusion machine was 2.0 mm), dried (493 K for 2 h) and then calcined at 773 K for 5 h. The heating rate of the furnace was maintained at 1 K/min. After grinding and sieving the extrudates, the created granulates with diameter of 1-2 mm were impregnated with an aqueous solution containing 3 wt% of ammonium metavanadate. After wet impregnation and evaporation of excess water, the catalysts were dried and calcined as described above. The impregnation and calcination procedures were repeated up to two or three times to obtain higher vanadia loadings. The resulting vanadia/titania (VT) catalysts were designated as VT-X-Y, where X refers to the type of titania support used in the preparation (A, B or C) and Y indicates the impregnated vanadia content (5, 10 or 15 wt%).

2.2. Characterization techniques

Inductively coupled plasma (ICP) analysis was carried out on a Spectroflame ICP-D spectrometer using two monochromators in the wavelength ranges of 165–460 and 240–790 nm, respectively. The samples were crushed and dissolved in an aqueous solution containing 4 vol% conc. H_2SO_4 and 10 vol% HF. The data were collected and processed with the Spectro Smart Analyzer Software (version 2.10).

Determination of surface area of the catalyst samples was performed by BET measurement on a Micromeritics ASAP 2000 analyzer. Prior to nitrogen adsorption, the samples were dried in vacuum at 573 K. The data were recorded and processed using the Micromeritics software ASAP 2010 (version 4.01).

Powder X-ray diffraction patterns of titania and vanadia/titania samples were collected on a Philips X'Pert Pro 3040/60 diffractometer using CuK_{α} radiation ($\lambda = 0.1542$ nm). Ni-filter and an X'celerator as detector which employs the real-time multiple strip (RTMS) detection technique were used. The powder diffraction patterns were collected in the 2 θ range of 15–95° with a step size of 0.017°, using a continuous scanning mode and with a scan time per step of 50 s. The XRD patterns were refined by employing the Rietveld refinement method [29] to determine the phase composition using the crystallographic data (both profile and structural parameters) of anatase and rutile titania. The average crystallite sizes of titania and vanadia were determined from the broadening of the XRD peaks corresponding to the (101), (110) and (001) reflections of anatase/rutile titania and vanadia respectively, using the Debye–Scherrer equation [30].

The structural stability of the catalyst samples (VT-A-10, VT-B-10 and VT-C-10) was determined by subjecting them to in situ high temperature powder XRD experiments. The high temperature XRD data were recorded with an Anton Paar HTK 1600 attachment. Alumina was used as a standard for calibration. A small amount of the sample was mounted on a platinum strip, which served as the sample stage as well as the heating element. A Pt/Rh-13% thermocouple spot-welded to the bottom of the stage was used to measure the temperature. The HT-XRD patterns were scanned in the 2θ range of 20–80° with a step size of 0.02° and a scan rate of 1°/min. The measurements were done in the temperature range of 298-623 K in static air with a heating rate of 10 K/min and a soaking time of 10 min. Variable temperature measurements were done at intervals of 25 K. All the experiments were performed in static air and the sample stage temperature was calibrated using thermal expansion of standard phase (α -Al₂O₃ standard from NIST, Gaithersburg, USA). Reflections from the Pt-strip sample holder have been used as an internal standard. This helps in determining the sample height-displacement error. These sample displacements at each temperature have been fixed for the refinement of parameters in the rutile and anatase titania phases. The XRD profiles were refined using the X'pert plus refining package provided by the Philips Co., to obtain the lattice parameters and phase composition.

Temperature-programmed desorption of ammonia (NH₃-TPD) was used to determine the acidities of the catalysts. For these investigations, a TPDRO 1100 with a thermal conductivity detector (TCD) of Thermo Finnigan was used. The evaluation of the data was carried out with the software-temperature-programmed desorbed oxidation and pulse chemisorption (version 2.3) of Thermo Electron.

⁵¹V Magic-angle spinning nuclear magnetic resonance (MAS-NMR) studies were carried out on a DSX 500 Bruker spectrometer. The spectra were recorded and processed with the Bruker software packages XWIN-NMR and Topspin 1.3.

Diffuse reflectance UV-visible (DRUV-vis) spectra of the dehydrated, powdered samples were recorded at 298 K on a Shimadzu UV-2500 PC spectrophotometer. The spectral features due to the support titania were subtracted from the spectra of the vanadia/titania catalysts by using the support itself as a reference material. For comparative studies spectra were also recorded using BaSO₄ as a reference material. The spectra consisted of several overlapping bands corresponding to different types of vanadium species. They were all deconvoluted and the vanadium species were quantified using the program Bruker WINEPR.

Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX spectrometer operating at X-band frequency ($\nu = 9.42$ GHz) and a 100 kHz field modulation. The spectra were recorded at 80 K using a Bruker BVTB 3500 variable temperature controller. The magnetic field was calibrated with a Bruker ER 035 M NMR gaussmeter. Microwave frequency was calibrated with a frequency counter fitted in the Bruker ER 041 XG-D microwave bridge unit. Spin Hamiltonian parameters were obtained by simulating the spectra using the Bruker Simphonia software package. The samples were taken in specially designed EPR quartz cells having a provision for adsorption/desorption studies. Prior to recording EPR spectra the samples were degassed at 623 K for 4 h.

2.3. Reaction procedure

The catalyst (8 g) was placed as a fixed-bed in a spiral coil reactor made of stainless steel. The inner diameter of the reactor was 6.0 mm, wall-thickness was 1.0 mm and reactor length was 1 m. The reaction temperature was 553 K and the absolute reaction pressure was 0.5 bar. β -Picoline was passed through the reactor with a WHSV of 1 h⁻¹. Air was used as oxidant and the feed was adjusted to generate an oxygen: β -picoline ratio of 1:1. The products were analyzed by gas chromatography (Siemens R GC 202;

Table 1	
Composition, average crystallite size, surface area and acidic properties of vanadia/titania cata	lysts

Catalyst ^a	V-loading Average crystallite size (XRD, nm)		tallite size (XRD, nm)	BET surface area (m	NH ₃ -TPD			
		(wt%)	Support	Vanadium oxide	Before extrusion	Before loading vanadium	After loading vanadium	(mmol/g _{cat})
VT-A-5	1.54	29	-	129	63	38	0.112	
VT-A-10	3.99	38	-	129	63	10	0.039	
VT-A-15	5.90	38	31	129	63	5	0.029	
VT-B-5	2.15	27	-	130	64	41	0.131	
VT-B-10	4.00	32	-	130	64	11	0.042	
VT-B-15	6.52	36	45	130	64	7	0.030	
VT-C-5	1.85	30	-	300	65	29	0.097	
VT-C-10	4.22	40	-	300	65	8	0.035	
VT-C-15	6.02	40	32	300	65	7	0.031	

Catalyst samples VT-A/B/C-10 and VT-A/B/C-15 were prepared by impregnating twice and thrice with ammonium metavanadate, respectively.



Fig. 1. XRD profiles of vanadia/titania catalysts. Reflections due to anatase and rutile phases are denoted as 'a' and 'r', respectively. Arrows indicate the reflections of crystalline V_2O_5 phase.

a 50 m FS-CW-20M column and a FID detector) and high performance liquid chromatography (Merck Hitachi with a UV–Vis L7420 detector and a Superspher 100 RP 18-4 μ column; solvent—ethanol; eluent—50 vol% H₂O and 50 vol% of a Na₃PO₄ buffer solution with pH 2.9). Operations were done at lower conversions to get a true correlation between catalytic activity and selectivity and the active site structure and concentration.

3. Results and discussion

3.1. Influence of vanadium loading on support structure—room and high temperature XRD studies

All the titania supports (A, B and C) used in this study were in anatase form. Calcination at high temperatures (873 K) influenced only their crystallite size and BET surface area (Table 1) but not their structural phase. However, the presence of vanadia influenced the phase of titania which was dependent on the type of the support (A, B and C) used. The vanadia/titania (VT) catalysts prepared using the type-B titania source had the anatase-type TiO₂ phase whereas those prepared using A and C-type titania materials contained a mixture of anatase and rutile phases (Fig. 1). The anatase form was prominent in VT-A-5 and VT-C-5 samples (vanadium contents in these samples were 1.54 and 1.85 wt%, respectively). On the other hand, VT-A-15 and VT-C-15, containing about 6 wt% vanadium, had predominantly the rutile phase (Fig. 1). At low concentrations, vanadium was in a highly dispersed state. A crystalline V₂O₅ phase (Fig. 1, corresponding XRD reflection indicated by arrows) was detected in the samples containing higher

Table 2										
Measured and	theoretical	crvstal	data (of	titania	in	vanadia/	titania	cataly	sts

	-			-
Sample	Phase	Unit cell pa	rameters (Å)	Volume of the
		а	С	unit cell (Å ³)
ICPDS21-1272 ^a	Anatase	3.785	9.514	136.30(1)
ICPDS21-1276 ^a	Rutile	4.593	2.959	62.42(2)
VT-A-10	Anatase	3.786	9.512	136.34(3)
	Rutile	4.581	2.959	62.36(7)
VT-B-10	Anatase	3.786	9.511	136.32(8)
VT-C-10	Anatase	3.783	9.505	136.02(6)
	Rutile	4.586	2.958	62.21(1)

^a Reference material.

amounts of vanadium (VT-A-15, VT-B-15 and VT-C-15). The crystallite size of anatase in VT-B-10 was 32 nm which was smaller than that of VT-A-10 (38 nm) and VT-C-10 (40 nm). While the compositions of the anatase and rutile phases in VT-A-10 were 58 and 42%, respectively, the anatase phase concentration was higher (68%) in the sample VT-C-10.

High temperature in situ XRD studies revealed that the catalysts are highly stable up to a temperature of 643 K. Crystallite size and phase composition did not vary appreciably at higher temperatures. The variations in anatase and rutile phase compositions were only marginal: 57–59% and 41–43% for VT-A-10 and 67–70% and 30–33% for VT-C-10, respectively.

Unit cell parameters of titania at 298 K in different samples compared well with those of the standard values (Table 2). The lattice had undergone thermal expansion with an increase in temperature. The unit cell volume of anatase increased from 136.34(3)



Fig. 2. DRUV-vis spectra of "neat" titania supports and vanadia/titania catalysts recording against BaSO4 as a reference material.

to 137.19(9) Å³ for VT-A-10, 136.32(8) to 136.10(1) Å³ for VT-B-10 and 136.02(6) to 136.90(8) Å³ for VT-C-10 as the temperature was increased from 298 to 598 K, respectively. The lattice or volume thermal expansion coefficient (α_v) values calculated from the unit cell volume according to a published formula [31] are $19.11 \times 10^{-6} \text{ K}^{-1}$, $18.06 \times 10^{-6} \text{ K}^{-1}$ and $19.88 \times 10^{-6} \text{ K}^{-1}$ in the temperature range of 298–623 K for anatase in samples VT-A-10. VT-B-10 and VT-A-10, respectively. The data obtained agree with that of the literature $(22.0 \times 10^{-6} \text{ K}^{-1} \text{ for anatase titania in the})$ temperature range 298–723 K) [31]. Similarly, the unit cell volume of rutile phase increased from 62.36(9) to 62.84(3) Å³ for VT-A-10 and 62.20(6) to 62.67(5) Å³ for VT-C-10. The lattice or volume thermal expansion coefficient (α_v) values calculated from the unit cell volume are 23.38×10^{-6} K⁻¹ and 23.19×10^{-6} K⁻¹ in the temperature range 298-623 K for rutile in VT-A-10 and VT-C-10 samples, respectively.

3.2. Nature and type of vanadium species—diffuse reflectance UV-vis spectroscopy

DRUV-vis spectroscopy is a powerful tool to elucidate the structure and types of vanadia species present in vanadia/titania catalysts. The potential of this technique has been used in great depth by Schoonheydt and co-workers [32] for the study of several supported vanadium oxide catalysts. Haller and co-workers [33] reported studies on vanadium-substituted mesoporous molecular sieves. The local environment of vanadium was investigated by comparing the results with the spectra of model compounds, which have a well-defined local symmetry. Among the model compounds, V2O5 has nearly square pyramidal geometry around vanadium consisting of four V-O bonds of similar length and a very short V=O bond. Metavanadates (PbV_2O_6 and ZnV_2O_6 , for example) have a structure consisting of strongly distorted octahedral pairs sharing corner oxygen atoms. Monomeric orthovanadates $(Na_3VO_4 \text{ and } Mg_3(VO_4)_2, \text{ for example})$ have a structure consisting of isolated tetrahedrally coordinated vanadium ions in a nearly symmetrical environment. Metavanadates such as NH₄VO₃, KVO₃ and NaVO₃ also have a tetrahedral environment, but strongly distorted and sharing two bridging oxygen atoms with other polyhedra. DRUV-vis spectra of vanadium oxides are characterized by ligand-to-metal ($0 \rightarrow V^{n+}$) charge transfer (CT) transitions and d-d transitions, when n = 4 or 3. With increasing coordination number the band maximum of the CT peak shifts to lower energy. Also with increasing polymerization the band broadens and shifts to lower energy.

The spectra of titania supports (A, B and C) along with those of the catalyst samples having different loadings of vanadium oxide (5-15%) recorded against BaSO₄ as a reference material are shown in Fig. 2. As seen from the figure, titania shows an intense CT band in the region 230-400 nm. The supported vanadia shows weak bands in the region 400-700 nm. Because of some overlap with the bands of the support titania, those of vanadium oxide are difficult to distinguish and quantify by using BaSO₄ as the reference material [18-28]. Hence, in further studies, we have used titania itself as a reference material and avoided spectral complications arising from the support. The support (A, B or C) used in the preparation of a particular catalyst was used as the reference material. As noted from the X-ray studies and textural properties (Table 1), the vanadia loading effected the phase and surface area of the support titania. Depending on the type of support (A, B or C), a part of titania was transformed from the anatase to the rutile phase. However, both of these structural forms of titania had similar spectral features. Thus, even if there was some structural transformation in the support due to the presence of vanadium that did not affect the spectral pattern. The contribution from the support was thus cancelled out by using titania itself as a reference material. Thus, the spectra reported in Fig. 3 are due to the supported vanadium oxide only and not to the support.

The asymmetric broad absorption in the region 400-700 nm (Fig. 3) indicates the presence of more than one type of vanadium oxide species. In order to estimate the type and concentration of the vanadium species, we have deconvoluted the DRUV-vis spectra. A representative deconvolution plot along with experimental and simulated curves for VT-A-10 is shown in Fig. 4. The satisfactory fit indicates that the broad, asymmetric UV-vis curve could be deconvoluted into five bands with band maxima at 397/403 (I). 440 (II), 472 (III), 550 (IV) and 668 (V) nm, respectively. The edge position, representative of the optical band gap energy, of these bands was determined in the classical fashion for the allowed transitions by finding the energy intercept of the straight line fitted through the low-energy rise in the plots of $[F(R_{\alpha}) \times h\nu]^2$ vs $h\nu$, where $F(R_{\alpha})$ is the Kubelka–Munk function for the infinitely thick sample and hv is the energy of the incident photon. The edge energy is sensitive to the coordination number and the structure of vanadium species. Monomeric tetrahedral VO_4^{3-} , polymeric tetrahedral VO₃⁻, square pyramidal V₂O₅ and distorted octahedral $V_2 O_6^{2-}$ species have UV edge energies (E_g) of 3.21, 3.20, 2.41 and 2.05 eV, respectively. From a comparison of the spectral data of vanadia/titania catalysts with those of the standard samples (Table 3), we conclude that the band I at 397/403 nm is due to monomeric tetrahedral VO₄³⁻ or polymeric distorted tetrahedral



Fig. 3. DRUV-vis spectra of vanadia/titania catalysts recorded against the support titania (A, B or C) as a reference material.



Fig. 4. Deconvoluted plots along with the experimental and simulated DRUV-vis spectra of VT-A-10.

Table 3

DRUV-vis spectral data and band assignments

Band width (nm)	UV edge	Type of	Type of vanadium species
width (iiii)	energy (ev)	transition	
3 45	2.72	LMCT	Tetrahedral VO ₄ ³⁻ and VO ₃ ⁻
60	2.42	LMCT	Square pyramidal V ₂ O ₅
80	2.22	LMCT	Distorted octahedral V ₂ O ₆ ²⁻
100	1.85	d-d	Square pyramidal V ⁴⁺
125	1.51	d-d	Square pyramidal V ⁴⁺
	Band width (nm) 3 45 60 80 100 125	Band UV edge energy (eV) 3 45 2.72 60 2.42 80 2.22 100 1.85 125 1.51	Band UV edge energy (eV) Type of transition 3 45 2.72 LMCT 60 2.42 LMCT 80 2.22 LMCT 100 1.85 d-d 125 1.51 d-d

 VO_3^- species. The bands II and III at 440 and 472 nm are due to V_2O_5 and $V_2O_6^{2-}$ -type species, respectively. A small part of vanadium on titania is reduced to +4 state. Bands due to vanadium +4 species (IV and V) appeared at 550 and 668 nm.

A number of conclusions would be drawn from the spectra and the deconvolution plots. The overall spectral intensity increased with vanadium content (Fig. 3). Spectral deconvolution indicated a marginal low energy shift of the band (I) at 397 to 403 nm. This shift in band position indicates formation of higher amounts of polymeric tetrahedral VO_3^- at higher vanadium concentrations. Samples with lower amount of vanadia (VT-A-5, VT-B-5 and VT-C-5) contained mainly the monomeric VO_4^{3-} species (397 nm). $V_2O_6^{2-}$ (472 nm; band III) and V^{4+} (550 and 668; bands IV and V) species were significant in the samples containing higher amounts of vanadia (Fig. 5).

3.3. Support-vanadia interactions: EPR spectroscopy

The catalyst samples showed weak EPR signals with resolved eight line hyperfine features especially in the parallel region. The intensity of the signals increased with increasing vanadium content and broadened at higher vanadia concentrations due to spinspin interactions (Fig. 6). In the preparation of catalysts, vanadium with +5 oxidation state (ammonium metavanadate) was used as the precursor. However, the final composition contained both +5and +4 type vanadium species. In other words, the support influenced and reduced a part of vanadium from +5 to +4 oxidation state. Quantitative estimation using VO(SO₄) as a reference sample indicated that only about 5% of total vanadium in VT-A-5 was reduced from the +5 to the +4 state while the majority of the vanadium was in +5 oxidation state. Only the reduced part of the vanadium showed EPR signals. Vanadium in the +5 state was detected by NMR spectroscopy. The EPR spectra were simulated using a rhombic spin Hamiltonian:

$$\mathcal{H} = \beta[g_{xx}B_{xx}S_{xx} + g_{yy}B_{yy}S_{yy} + g_{zz}B_{zz}S_{zz}] + [A_{xx}S_{xx}I_{xx} + A_{yy}S_{yy}I_{yy} + A_{zz}S_{zz}I_{zz}],$$
(1)

where β is the Bohr magneton; (B_{xx} , B_{yy} and B_{zz}) and (g_{xx} , g_{yy} and g_{zz}) are the magnetic field and *g*-parameters along *x*, *y* and *z* directions, respectively; *S* is the electron spin angular momentum with the components being S_{xx} , S_{yy} and S_{zz} along the *x*, *y* and *z* directions, respectively. The spin Hamiltonian parameters are listed in Table 4. The rhombic spin Hamiltonian parameters indicate a low-symmetry environment around vanadium(IV) in vanadia/titania catalysts. The spectra of the VT-C series are broader and more complicated than those of the VT-A series, indicating higher amounts of agglomerated vanadium in the former series of catalysts (Fig. 6).

The reducibility of vanadium was investigated by treating the samples with dry-hydrogen. After reduction at elevated temperatures, the intensity of the EPR signals due to isolated vanadium species (in VT-A-5) decreased. A broad background signal appeared indicating formation of clustered and interacting-type V^{4+}/V^{3+} species (Fig. 7). Also during the oxidation reaction of β -picoline, larger quantities of V^{4+} species have formed. The EPR spectrum of the spent catalyst is shown in Fig. 8. The hyperfine features were completely lost and only an intense broad signal was ob-



Fig. 5. Variation in the areas of UV-vis bands corresponding to different vanadium oxide species as a function of vanadium content in vanadia-titania catalysts: (i) VT-A and (ii) VT-C. Band I (397/403 nm; monomeric tetrahedral VO_{4}^{3-} /polymeric distorted tetrahedral VO_{3}^{-}), band II (440 nm; V_2O_5), band III (472 nm; $V_2O_6^{2-}$), band IV (560 nm, V^{4+}) and band V (668 nm, V^{4+}).

EPR spin Hamiltonian parameters of vanadia/titania catalysts									
Catalyst	g _{xx}	g_{yy}	g _{zz}	A_{xx} (G)	A_{yy} (G)	A_{zz} (G)			
VT-A-5/10/15	1.980	1.975	1.928	57.0	60.0	178.0			
VT-B-5	1.978	1.975	1.926	57.0	65.0	180.0			

1.933

58.0

60.0

1.978

1.983



Fig. 6. X-band EPR spectra of vanadia/titania catalysts as a function of vanadium concentration.

served corresponding to formation of larger amounts of interacting V⁴⁺ species during the oxidation reactions. Titania is a reducible oxide. However, such a reduction of titanium from +4 to +3 state was not observed under our experimental conditions.

3.4. Acidic properties of the catalysts-NH₃-TPD

Temperature-programmed desorption of ammonia (NH₃-TPD) was used to investigate changes in the acidic properties of the materials. As shown in Fig. 9 and Table 1, the amount of highly acidic sites decreased strongly when the support material was impregnated with NH₄VO₃ a second or a third time. The amount of acidic sites did not depend on the catalyst surface area (Table 1). The TPD results show very strong similarities for the higher loaded materials (VT-X-10 and -15). A real difference can only be found for the



Fig. 7. EPR spectra of vanadia/titania catalyst (VT-A-5) treated with dry-hydrogen at elevated temperatures.



Fig. 8. EPR spectra of fresh and spent catalysts: VT-A-15.



Fig. 9. NH₃-TPD of vanadia/titania catalysts.

catalysts, which had been impregnated only once. A calculation of the amount of desorbed NH₃ per surface area shows similar values for VT-B-5 and VT-C-5, while VT-A-5 displays a lower acidity. A comparison to NH₃-TPD measurements of the pure support materials (not shown here) revealed a strong decrease of highly acidic sites for all materials. This indicates that surface acidity depended mostly on the vanadium loading.

3.5. Nature and type of vanadium species—⁵¹ V MAS NMR studies

Catalysts VT-A-5, 10 and 15, as well as VT-B-10 and VT-C-10 were characterized using magic-angle spinning (MAS) NMR techniques. The NMR spectrum of VT-A-5 shows two main peaks. One, with a δ_{iso} of -615 ppm in our spectra, has been attributed to polycrystalline V₂O₅ in the literature [2,34,35], while the second one, at about 640 ppm, can be assigned to strongly bound vanadium, which has a distorted octahedral oxygen environment. The

complexity of the NMR signal indicates the presence of other species, but these are too weak to be clearly identified.

The NMR spectra of all catalysts with higher vanadium loadings (see VT-A-10 and VT-A-15 as examples in Fig. 10) are far less complex. Here, only the peak assigned to bulk V_2O_5 is visible. MAS NMR spectroscopy is not able to identify other vanadium oxide species here. It has to be assumed that vanadium oxide completely covers the surface in multiple layers. Spectra from VT-B-10 and VT-C-10 showed the same result and are not presented here. The intense NMR signals indicate that vanadium in vanadia–titania catalysts is mainly in the +5 oxidation state.

3.6. Catalytic activity—oxidation of β -picoline

The catalytic activity of all previously described catalysts in the oxidation of β -picoline to nicotinic acid was investigated. Byproducts found in this reaction included pyridine-3-carbaldehyde and maleic acid. The neat supports alone could not catalyze the reaction. Turnover frequencies (TOF; Table 5) were estimated based on the total amount of vanadium present in the catalyst as well as the active vanadium sites (monomeric + polymeric tetrahedral vanadium). The concentration of the active vanadium sites (Table 5) was determined from the DRUV-vis spectroscopy and spectral deconvolution. An assumption is made that the ratio of the areas of the deconvoluted bands corresponds to the ratio of the concentration of the corresponding vanadium species. The TOF values estimated based on the active vanadium sites are higher by two to three times than those estimated based on the total vanadium content in the catalyst. As shown in Table 5, experiments with catalysts VT-A-5, VT-B-5 and VT-C-5 show the highest catalytic activity. At the reaction conditions used here, the conversion and TOF seem to be proportional to the catalyst's BET surface area. With these three catalysts, high amounts (19.0 to 27.4%) of the side product maleic acid were found as well. This may be due to the fact that the reaction is highly exothermic, so at higher conversions the side reaction is accelerated. The other catalysts lead to lower conversions (1.2-3.1%), but only the aldehyde and nicotinic acid were observed as products. The decomposition product maleic acid was not found, and the percentage of aldehyde in the reaction products increased. A comparison of the different support materials shows a nearly linear dependency of conversion and TOF on BET surface areas, independently of the support material used. The acidity of support material or loaded catalyst showed no correlation to the conversions and selectivities observed. It can be deduced that the increase of the vanadium loading, at least when it is as high as in these experiments, has no positive effect on the conversion. A similar observation can be made for the selectivity to nicotinic acid. Selectivity decreases with increasing vanadium content of the catalysts. A direct comparison of the catalvsts shows little difference in the product selectivities obtained using catalysts with high vanadium loadings. Therefore, while the pure support material is inactive for the reaction, repeated impregnation and calcination cycles of the support material is detrimental to both conversion and selectivity to the desired products. It may be noted that the TOF values for oxidation of β -picoline are comparable those reported for the selective catalytic reduction (SCR) of NO by NH₃ over these catalysts [23].

3.7. Active vanadium species and structure-function relationships

The composition of the anatase phase varies almost linearly with the BET surface area. Further, the catalytic activity for β picoline oxidation correlates with the anatase phase content of the catalysts (Fig. 11i). Hence, the structure of the support has a significant bearing on the catalytic oxidation activity [36]. DRUV-vis spectra revealed that there exist different types of vanadia species



Fig. 10. ⁵¹V MAS NMR of VT-A-5, -10 and -15.

Table 5

Catalytic activity of the different vanadia–titania catalysts in β -picoline oxidation with molecular oxygen^a

Catalyst ^b	Conversion	Turnover freque	ency (TOF, h^{-1})	Product selectivity	Yield of		
	of β-picoline (%)	Per mol of vanadium ^c	Per mol of (monomeric + polymeric) T _d vanadium ^d	Pyridine-3- carbaldehyde	Maleic acid	Nicotinic acid	nicotinic acid (%)
VT-A-5 (42.1)	10.3	3.7	8.7	20.4	27.4	52.2	5.4
VT-A-10 (30.4)	1.9	0.3	0.9	59.5	0	40.5	0.8
VT-A-15 (30.5)	1.2	0.1	0.3	59.4	0	40.6	0.5
VT-B-5 (34.3)	11.3	2.9	8.4	20.3	23.5	56.2	6.3
VT-B-10 (40.0)	3.1	0.4	1.1	67.8	0	32.2	0.5
VT-B-15 (34.6)	2.0	0.2	0.5	63.1	0	36.9	0.7
VT-C-5 (31.9)	6.5	1.9	6.0	29.2	19.0	51.8	3.4
VT-C-10 (35.6)	2.3	0.3	0.8	57.4	0	42.6	1.0
VT-C-15 (27.5)	1.9	0.2	0.6	53.3	0	46.7	0.9

^a Reaction conditions: Oxygen/ β -picoline ratio = 1, WHSV = 1 h⁻¹, pressure = 0.5 bar, temperature = 353 K.

^b Values in parentheses indicate percentage of active (monomeric + polymeric $T_{\rm d}$) vanadium sites estimated from DRUV-vis spectral data.

^c TOF = moles of β -picoline converted per mole of vanadium per hour. ^d TOF = moles of β -picoline converted per mole of active (monomeric + polymeric T_d) vanadium sites.



Fig. 11. Correlation of β-picoline oxidation activity with (i) specific surface area (S_{BET}) and anatase composition, and (ii) concentration of tetrahedral vanadium species.

on the surface of vanadia/titania catalysts. There is a correlation (Fig. 11ii) between the oxidation activity and the concentration of (monomeric + polymeric) tetrahedral vanadium oxide species (397 and 403 nm). The latter was estimated based on the areas of the corresponding UV-vis bands. The higher the concentration of these tetrahedral vanadium oxide species the higher was the β -picoline oxidation activity. Catalysts with higher amount of vanadium contained predominant amounts of inactive square pyramidal V2O5 (440 nm) and octahedral $V_2O_6^{2-}$ (472 nm) species (Fig. 5), and as a consequence catalytic activity was low over these catalysts. As the concentration of vanadium increased, the band at 397 nm had shifted to 403 nm. This shift in band position associated with a shift in the UV edge energy from 2.74 to 2.72 eV indicated the formation of polymeric type tetrahedral vanadium oxides. While both these vanadium oxides are active in β -picoline oxidation. the latter having a distorted tetrahedral geometry is more selective and yields the desired products-picolinaldehyde and nicotinic acid. Vanadium in the +5 oxidation state is the active precursor. Thus, this study reveals that high surface area, anatase phase titania and dispersed, polymeric, distorted tetrahedral vanadium oxide species are the determining factors leading to highly efficient and selective vanadia/titania catalysts. The tetrahedral VO_3^- and VO_4^{3-} (397 and 403 nm) are the active species in the selective catalytic oxidations over vanadia/titania catalysts.

4. Conclusions

Vanadia/titania catalysts with varying vanadium content were prepared using three different titania carrier materials. The structure of titania changed from the anatase to the rutile phase during the preparation of the catalysts. This change in phase composition depended on the vanadium content and the source and acidity of the titania material. The active vanadium sites in these catalysts in β -picoline oxidation were investigated by XRD and DRUV-vis, EPR and ⁵¹V MAS NMR spectroscopy techniques. The catalysts contained at least five different types of vanadium oxide species viz., monomeric tetrahedral VO_4^{3-} (397 nm), polymeric distorted tetrahedral VO_3^- (403 nm), square pyramidal V_2O_5 (440 nm), octahedral $V_2O_6^{2-}$ (472 nm) and V^{4+} oxide (550 and 668 nm) species. While both VO_4^{3-} and VO_3^{-} species (397 and 403 nm) are active in β -picoline oxidation, the latter with a distorted tetrahedral geometry, yields the desired products (picolinaldehyde and nicotinic acid). High surface area, anatase structure and dispersed, distorted tetrahedral vanadium oxide species lead to more active and selective oxidation catalysts.

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