

# $^{51}\text{V}$ and $^1\text{H}$ solid-state MAS NMR studies of vanadia catalysts supported on $\text{Al}_2\text{O}_3\text{--TiO}_2$ sol–gel mixed oxide

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## Abstract

A series of vanadia catalysts supported on sol–gel derived mixed oxide  $\text{Al}_2\text{O}_3\text{--TiO}_2$  were synthesized with a  $\text{V}_2\text{O}_5$  content varying from 1 to 25 wt.%. The catalysts were characterized by employing  $^{51}\text{V}$ ,  $^{27}\text{Al}$ ,  $^1\text{H}$  MAS NMR, diffuse reflectance FT-IR and BET surface area measurements. In the calcined catalysts  $^{51}\text{V}$  NMR studies indicated the peaks corresponding isolated and distorted tetrahedral vanadia species at low  $\text{V}_2\text{O}_5$  contents and octahedral vanadia species at high vanadia loadings. Upon outgassing the catalysts, a decrease in the intensity of the peak corresponding to distorted tetrahedral species was observed with a consequent increase in the intensity of the peak corresponding to isolated tetrahedral vanadate species due to the removal of water molecules or hydroxyl groups from the coordination sphere of vanadium. The  $^1\text{H}$  MAS NMR studies showed the presence of terminal and bridged hydroxyl groups of alumina and titania in the  $\text{Al}_2\text{O}_3\text{--TiO}_2$  mixed oxide support. The overtone bands corresponding to  $\text{V}=\text{O}$  were seen only at higher vanadia contents in the DRIFT spectra of the catalysts. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Vanadia; Alumina–titania; Solid-state NMR; DRIFT

## 1. Introduction

Vanadia catalysts supported on composite supports such as modified and mixed oxides were employed earlier for catalyzing reactions such as partial oxidation and selective catalytic reduction of  $\text{NO}_x$  [1–6]. In comparison to single component support materials, the composite oxide supports were found to exhibit higher surface area, surface acidity, thermal and mechani-

cal strength [7]. Handy et al. [5] and Baiker et al. [6] attributed the increased activities of the vanadia catalysts supported on mixed oxides to the high surface areas of the mixed oxides allowing immobilization of higher amounts of active phase, i.e.,  $\text{V}_2\text{O}_5$ , without the formation of microcrystallites. The synthesis and characterization of titania–alumina mixed oxides using different preparative techniques such as coprecipitation, sol–gel technique etc., were reported by various investigators [8–10]. Molybdena catalysts supported on titania modified alumina were found to exhibit high catalytic activities in hydrotreating reactions [11,12]. Vanadia cata-

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lysts supported on titania-alumina mixed oxide and titania modified alumina were found to exhibit superior activities in selective catalytic reduction of  $\text{NO}_x$  [13–16].  $^{51}\text{V}$  solid-state NMR has been used by various investigators to differentiate between different kinds of vanadia species in the catalysts [16–22]. The types of vanadia species were found to depend upon the precursor used, chemical nature of the support, method of preparation and type of pretreatment, e.g. evacuation of the catalysts prior to recording the spectra. Mastikhin et al [16,17] in their  $^{51}\text{V}$ ,  $^1\text{H}$  solid-state NMR studies on vanadia catalysts supported titania modified alumina/silica observed vanadia species in interaction with both the components of the modified oxide. Similarly, our  $^{51}\text{V}$  NMR studies [18] on vanadia catalysts supported on zirconia–silica mixed oxide indicated vanadia species in interaction with both zirconia and silica components of the mixed oxide support. Eckert and Wachs [19] in their  $^{51}\text{V}$  NMR studies on  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  and  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts have noticed tetrahedral vanadia species at low  $\text{V}_2\text{O}_5$  contents and distorted octahedral vanadia species at higher vanadia loadings. The tendency for formation of octahedral vanadia species was found to be high in the case of titania supported vanadia catalysts in comparison to  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  catalysts. Iyer et al. [20] in their  $^{51}\text{V}$  wide-line NMR studies on vanadium contaminated aluminas and aluminosilicate gels observed distorted tetrahedral vanadium species ( $\text{Q}^2$  type) at low vanadia contents and six coordinate species at high  $\text{V}_2\text{O}_5$  loadings. Lapina et al. [21] in their  $^{51}\text{V}$  NMR studies on  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  observed the presence of two kinds of tetrahedral vanadia species at low loadings and distorted octahedral vanadia species and at high  $\text{V}_2\text{O}_5$  contents. It was observed that upon outgassing the samples the resonance corresponding to distorted tetrahedral species considerably decreased in intensity and the peak corresponding to isolated tetrahedrally coordinated vanadate species was observed due to the removal of water molecules or hydroxyl groups from the former species.

$^1\text{H}$  MAS NMR was being employed as a complementary technique to IR, for determining various kinds of hydroxyl groups in the supports and catalysts. In alumina, five resonances corresponding to terminal or basic and bridged or acidic hydroxyl groups coordinated to tetrahedral or octahedral Al were observed [23,24].  $^1\text{H}$  MAS NMR investigations were reported on zirconia modified silica, titania modified alumina/silica to determine the types of hydroxyl groups [16,17,25]. Mastikhin et al. [16,17] in their  $^1\text{H}$  MAS NMR studies on vanadia catalysts supported on titania modified alumina/silica, showed that interaction of active vanadia phase with both terminal and bridged hydroxyl groups of the support material takes place. The  $^1\text{H}$  MAS NMR studies on vanadia catalysts supported on  $\text{ZrO}_2\text{--SiO}_2$  sol–gel mixed oxide and mixed oxide supports were reported in our earlier investigations [18,26].

FT-IR spectroscopy was found to provide useful information about various kinds of hydroxyl groups in the supports and the catalysts, and also different types of vanadia species in the catalysts [27,28]. The vibrations corresponding to tetrahedral vanadia species were usually observed in the region  $930\text{--}950\text{ cm}^{-1}$  at lower concentrations of  $\text{V}_2\text{O}_5$ , and the vibrations corresponding to decavanadate species were seen in the region  $940\text{--}1020\text{ cm}^{-1}$  at monolayer loadings of vanadia and the vibrations corresponding to  $\nu_{\text{V=O}}$  at  $1020\text{ cm}^{-1}$  and  $\text{V--O--V}$  at  $\sim 740\text{ cm}^{-1}$  were usually observed at high loadings of the active phase [27,28]. In the case of catalysts with the supports which are transparent in the skeletal vibration region ( $700\text{--}1300\text{ cm}^{-1}$ ), the observance of IR bands in the overtone region ( $1900\text{--}2200\text{ cm}^{-1}$ ) was found to give important information regarding the presence of monolayer vanadia species. In the present investigation, we report the synthesis and characterization of the alumina–titania sol–gel mixed oxide supported vanadia catalysts, employing  $^{51}\text{V}$ ,  $^{27}\text{Al}$ ,  $^1\text{H}$  MAS NMR and diffuse reflectance FT-IR spectroscopy and BET surface area measurements.

## 2. Experimental

$\text{Al}_2\text{O}_3$ – $\text{TiO}_2$  mixed oxide was synthesized with a 1:1 molar ratio using 2,4-pentanedione as the complexing agent. The details of the preparation are given elsewhere [26]. The typical procedure of the synthesis of mixed oxide is as follows; 0.1 mol each of the aluminum tri-*sec*-butoxide (ATSB) and titanium tetrapropoxide (TTP) precursors were dissolved in 200 ml of *n*-butanol followed by heating at 70°C to get a clear solution. The complexing agent 2,4-pentanedione (0.5 mol) was added to this clear solution prior to hydrolysis with 4.2 mol of water per mol alkoxide. Transparent gels were obtained in all cases and were aged at ambient temperature for 12 h. The solvents were removed at 110°C and after drying the materials were finely powdered and then calcined at 500°C to remove the organic residues.

A series of catalysts with vanadia contents varying between 1–25 wt.% were prepared by impregnating alumina–titania support with a methanolic solution of vanadium(III) acetylacetonate (Gelest). Methanol was evaporated slowly to dryness in a rotary evaporator. The resulting material was dried at 110°C overnight followed by calcination at 500°C for 5 h. The vanadia contents of the catalysts were estimated by Inductively Coupled Plasma (ICP) analysis using Perkin Elmer Optima 3300 DV ICP-OES spectrometer after calibrating the instrument with

NIST traceable standards. A weighed sample was digested in hot concentrated nitric acid until the dissolution was complete and then the solution was diluted to ~2% (V/V  $\text{HNO}_3$ ) prior to analysis.

BET surface areas were determined using Coulter SA 3100 instrument and an automated gas volumetric method employing nitrogen as the adsorbate at  $-196^\circ\text{C}$ . Samples were out-gassed under vacuum at 200°C for 1 h immediately prior to analysis. Pore size distributions and pore volumes were measured by using BJH method.  $^{51}\text{V}$ ,  $^{27}\text{Al}$ ,  $^1\text{H}$  and MAS NMR experiments were carried out on a Bruker Avance DPX 300 multinuclear FT-NMR instrument. A standard bore Bruker MAS/CPMAS probe with 4 mm zirconia rotors was used. The samples were dehydrated at 350°C for 30 min in He flow prior to recording the spectra.  $^{51}\text{V}$  static and MAS spectra were obtained at 78.9 MHz with a pulse length of 1  $\mu\text{s}$  and relaxation delays of 1 s over a spectral window of 149 kHz. Chemical shifts were referenced to external  $\text{VOCl}_3$ , using  $\text{V}_2\text{O}_5$  ( $\delta = -320$  ppm) as a secondary reference. MAS spectra were recorded by variable spinning speeds ranging from 6 to 10 kHz.  $^{27}\text{Al}$  MAS NMR spectra were obtained at 78.21 MHz with a 30° pulse width of 2  $\mu\text{s}$  and 250 ms delay between pulses and a spectral range of 50 kHz. All the spectra were referenced to external aqueous aluminum nitrate ( $\delta = 0$  ppm). The samples are spun at 10 kHz in air and typically

Table 1  
BET surface areas and vanadia contents of the catalysts

Catalyst $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ – $\text{TiO}_2$	Catalyst code	$\text{V}_2\text{O}_5$ (wt.%) <sup>a</sup>	Surface area ( $\text{m}^2/\text{g}$ )
$\text{Al}_2\text{O}_3$ – $\text{TiO}_2$	Al–Ti	–	304
1	V/Al–Ti 1	0.5	298
2	V/Al–Ti 2	0.9	292
3	V/Al–Ti 3	1.3	288
4	V/Al–Ti 4	4.2	283
5	V/Al–Ti 5	7.9	279
6	V/Al–Ti 6	11.4	274
7	V/Al–Ti 7	14.1	126
8	V/Al–Ti 8	24.4	146

<sup>a</sup>Estimated from ICP analysis.

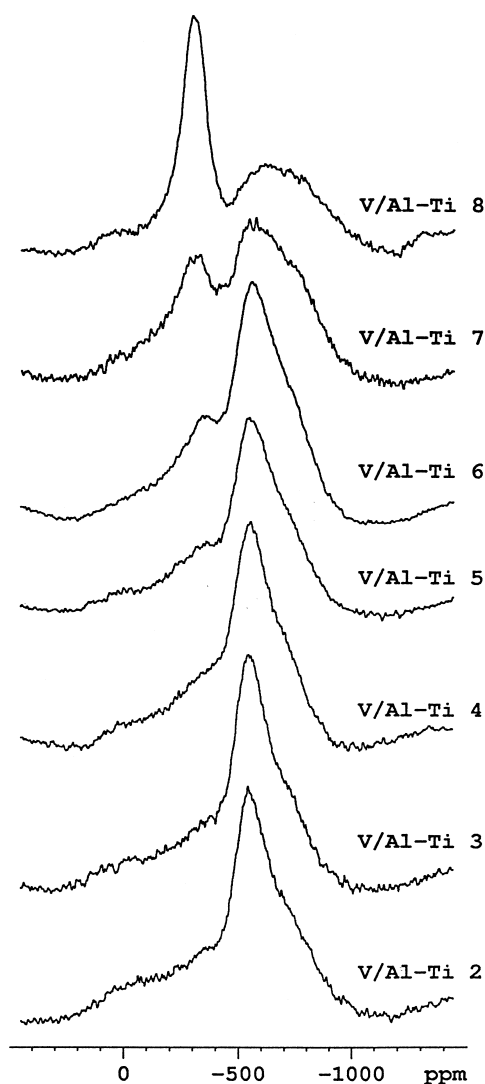


Fig. 1.  $^{51}\text{V}$  solid-state NMR spectra of the calcined catalysts.

540 FIDs were collected for each sample.  $^1\text{H}$  MAS NMR spectra were recorded at 300 MHz with a  $30^\circ$  pulse length of  $3\ \mu\text{s}$  with 1 s delay between the pulses over a spectral window of 12 kHz. The chemical shifts in ppm were referenced to external TMS using neat *p*-dioxane as secondary reference. The samples were spun at 10 kHz and 124 FIDs were accumulated for each sample. Prior to recording of the spectra the samples were outgassed at  $350^\circ\text{C}$  for 30 min in a flow of He and immediately transferred to zirconia rotors. DRIFT spectra were acquired

using a SPECTRA TECH DRIFT accessory 'THE COLLECTOR' in an ATI Mattson Research Series FT-IR spectrometer.

### 3. Results and discussion

The BET surface areas of the catalysts and vanadia contents estimated from ICP analysis are given in Table 1. It can be seen from Table 1 that there is a decrease in the surface area of  $\text{Al}_2\text{O}_3\text{-TiO}_2$  mixed oxide upon with vanadia impregnation. This behavior is expected due to the blockage of the pores of the support with the active component. The high surface area of  $304\ \text{m}^2/\text{g}$  of alumina–titania allows immobilization of higher amounts of dispersed vanadia phase without the formation of microcrystallites. The  $^{51}\text{V}$  NMR and DRIFT studies of the catalysts as discussed below are in support with this statement.

Fig. 1 shows the  $^{51}\text{V}$  solid-state NMR spectra of the calcined catalysts. The chemical shifts are given in Table 2. Two peaks at  $-550$  and  $-350$  ppm, respectively, can be seen in the spectra. The resonance at  $\sim -550$  ppm can be assigned to tetrahedral vanadia species. The broadness of the peak suggests the distorted environment of oxygen atoms around tetrahedral vanadia species. The peak at  $\sim -310$  ppm observed at higher loadings in the samples V/Al–Ti 7 and 8, can be assigned to distorted octahedral vanadia species. Lapina et al. [21] in their  $^{51}\text{V}$  NMR studies on calcined  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  catalysts have assigned the peak at  $-520$  to

Table 2  
 $^{51}\text{V}$  NMR chemical shifts of the catalysts

Catalyst	$\delta_{\text{ppm}}$ calc. catalysts	$\delta_{\text{ppm}}$ evac. catalysts
V/Al–Ti 3	–547	–
V/Al–Ti 4	–350, –553	–439, –747
V/Al–Ti 5	–350, –557	–443, –728
V/Al–Ti 6	–340, –548	–441, –753
V/Al–Ti 7	–309, –572	–300, –446, –751
V/Al–Ti 8	–303, –578	–302, –740

–590 ppm to vanadium atoms in distorted tetrahedral environment with water molecules in the coordination sphere of vanadium, the peak at –750 ppm to isolated  $\text{VO}_4^{3-}$  tetrahedra and the peak at –350 ppm was attributed to polynuclear vanadium species in distorted octahedral environment. The distorted tetrahedral species ( $\delta = -520$  ppm) were found to result in the formation of isolated tetrahedral ( $\delta = -750$  ppm) species due to the removal of water molecules upon dehydration treatments of the samples. Fig. 2 shows the  $^{51}\text{V}$  solid-state NMR spectra of the catalysts evacuated at  $350^\circ\text{C}$  for 30 min. The chemical shifts are given in

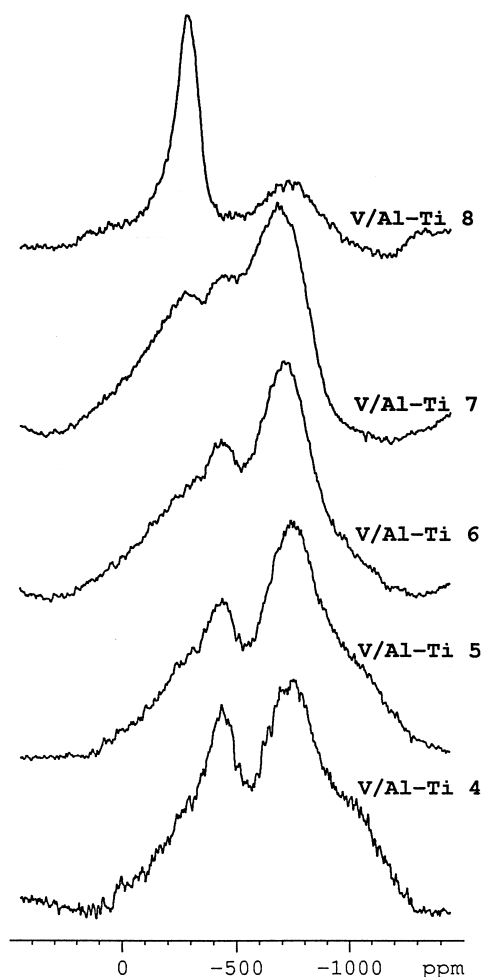


Fig. 2.  $^{51}\text{V}$  solid state NMR spectra of the catalysts evacuated at  $350^\circ\text{C}/30$  min.

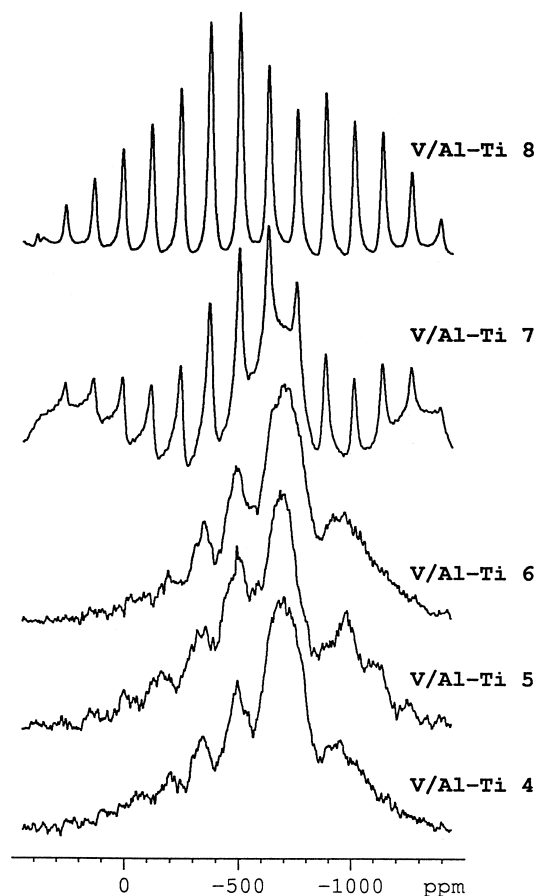


Fig. 3.  $^{51}\text{V}$  MAS NMR spectra of the catalysts evacuated at  $350^\circ\text{C}/30$  min (spin rate 10 kHz).

Table 2. The  $^{51}\text{V}$  resonances were either very weak or absent in the catalysts with very low vanadia contents, even after acquiring many number of scans. In the samples V/Al-Ti 4, 5 and 6, the peak at  $\sim -440$  ppm can be assigned to distorted tetrahedral vanadium species and the peak at  $\sim -740$  ppm can be attributed to isolated tetrahedral  $\text{VO}_4^{3-}$  species. The latter species might have formed at the expense of the peak at  $-550$  ppm [21]. The peak at  $\sim -350$  ppm which was observed in the calcined samples disappeared upon evacuation in these samples with the appearance of new peak at  $-440$  ppm. The peak at  $-440$  ppm might be formed by the removal of water molecules or hydroxyl groups from distorted octahedral species. Lap-

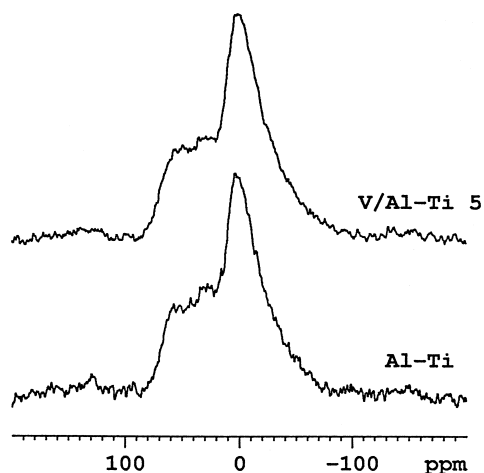


Fig. 4.  $^{27}\text{Al}$  MAS NMR spectra of the Al-Ti support and catalyst (spin rate 10 kHz).

ina et al. [22] in their  $^{51}\text{V}$  NMR studies on vanadia catalysts supported on titania-silica have noticed the formation of octahedral vanadia species upon hydration of the tetrahedral species ( $\delta = -460$  ppm). The peak at  $-440$  ppm gradually decreased in intensity with increase in vanadia content in the samples. In the evacuated samples V/Al-Ti 4, 5 and 6, the peaks corresponding to isolated and distorted tetrahedral vanadia species were observed at  $-740$  and  $-440$  ppm. In the sample V/Al-Ti 7 an additional the peak corresponding to distorted octahedral vanadia species could be seen at  $-300$  ppm and in the sample V/Al-Ti 8, this peak is more prominent. In the V/Al-Ti 8 sample the peak at  $-440$  ppm disappeared and intensity of  $-740$  ppm peak decreased, showing an increase of octahedral vanadia sites and a decrease in tetrahedral vanadia species. In situ laser Raman spectroscopic studies by Wachs [29] and Machej et al. [30] on supported vanadia catalysts also revealed that the nature of surface vanadium oxide species will depend on the pretreatment conditions of the catalysts. A broad Raman band at  $\sim 990$   $\text{cm}^{-1}$  was observed at ambient conditions in the calcined samples which was attributed to distorted octahedral surface vanadyl species. In the dehydrated samples a shift in Raman frequencies was observed to

higher wavenumbers  $\sim 1020$ – $1030$   $\text{cm}^{-1}$  corresponding to isolated tetrahedral vanadate species. Dehydrating the samples in-situ prior to recording the spectra was found to change the coordination of surface vanadia species from octahedral to tetrahedral species.

$^{51}\text{V}$  MAS NMR spectra of the catalysts acquired at a spin rate of 10 kHz are shown in Fig. 3. It can be seen from the figure that there is not much influence of MAS on the width of the peaks at lower loadings, which may be due to wide chemical shift distribution. This behavior was explained due to large quadrupole coupling constants and chemical shift parameters [19–21]. Thus the  $^{51}\text{V}$  MAS NMR studies of

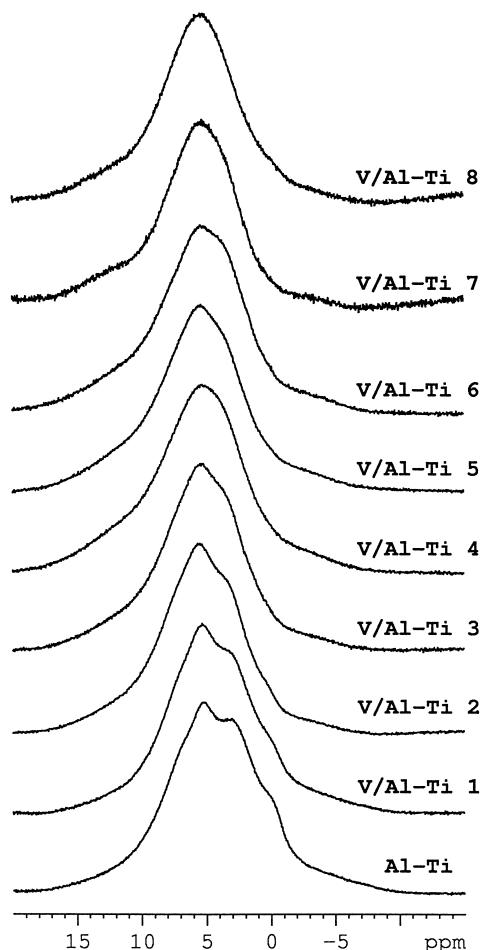


Fig. 5.  $^1\text{H}$  MAS NMR spectra of the catalysts evacuated at  $350^\circ\text{C}/30$  min (spin rate 10 kHz).

lower loaded samples V/Al–Ti 4, 5 and 6 indicate highly dispersed tetrahedral vanadia species and amorphous aggregates of  $V_2O_5$  in the case of V/Al–Ti 7 and V/Al–Ti 8 samples with high  $V_2O_5$  contents.

$^{27}Al$  MAS NMR spectra of the Al–Ti support and the V/Al–Ti 3 catalyst are shown in Fig. 4. Three resonances corresponding the 4, 5 and 6 coordinated alumina were observed at 52, 30 and 3 ppm, respectively. In our earlier investiga-

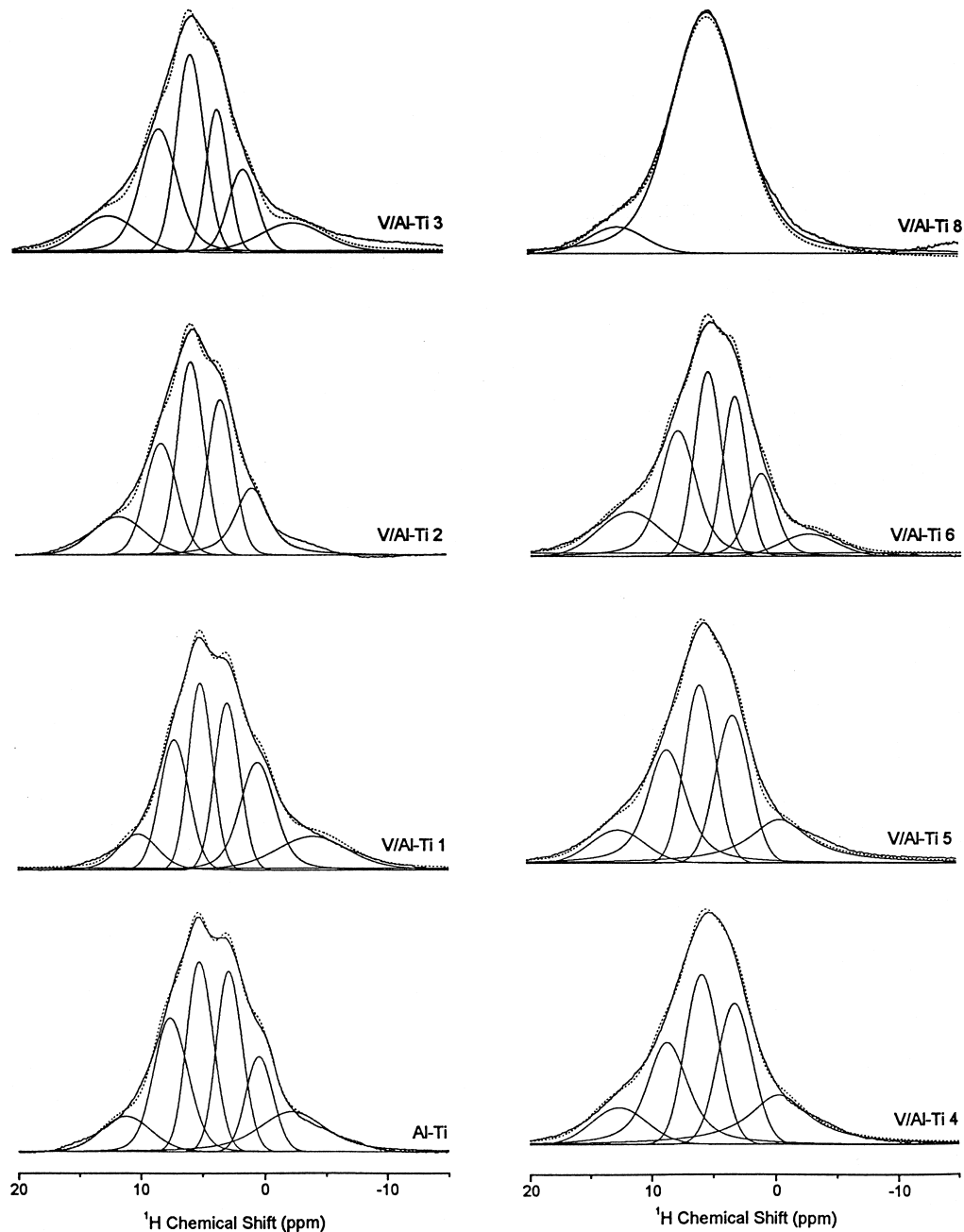


Fig. 6. The deconvoluted  $^1H$  MAS NMR spectra of the Al–Ti and V/Al–Ti catalysts. (—) Experimental spectrum; (---) Curve fitted spectrum.

tion [26] we reported the  $^{27}\text{Al}$  spectra of the calcined  $\text{Al}_2\text{O}_3\text{-TiO}_2$  mixed oxide. In the present study the samples outgassed at  $350^\circ\text{C}$  exhibited a decrease in the intensity of the 5 coordinated Al peak which may be due to the removal of water molecules to form 4 coordinated alumina.

The  $^1\text{H}$  MAS NMR spectra of the  $\text{Al}_2\text{O}_3\text{-TiO}_2$  support and the catalysts are given in Fig. 5. The spectra were deconvoluted into Voigt line shapes using the GRAMS/32 software and are given in Fig. 6. Mainly five kinds of hydroxyl groups with the peaks at  $-0.3$ ,  $3.0$ ,  $5.5$  and  $7.6$  ppm were observed in the  $\text{Al}_2\text{O}_3\text{-TiO}_2$  mixed oxide. The peak at  $-0.3$  ppm can be attributed to the terminal/basic hydroxyl groups (basic OH) coordinated to octahedral alumina [23,24]. The peaks at  $3.0$  and  $5.5$  ppm may correspond to overlapping resonances from Al-OH and Ti-OH hydroxyl groups. The peak at  $7.0$  ppm is typical of bridged hydroxyl groups (Ti-OH-Ti) of titania or bridged hydroxyl groups between alumina and titania, i.e., Ti-OH-Al groups [16]. In earlier  $^1\text{H}$  MAS NMR investigations [23,24] on alumina, the peaks at upfield were attributed to terminal or basic hydroxyl groups and the peaks at downfield were attributed to acidic or bridged hydroxyl groups. Similar assignment was made by Mastikhin et al. [16] in their  $^1\text{H}$  MAS NMR studies on  $\text{V}_2\text{O}_5$  catalysts supported on titania modified alumina. It can be seen from Fig. 5 that with increase in vanadium loading there is a decrease in the intensity of the resonance at  $-0.3$  ppm corre-

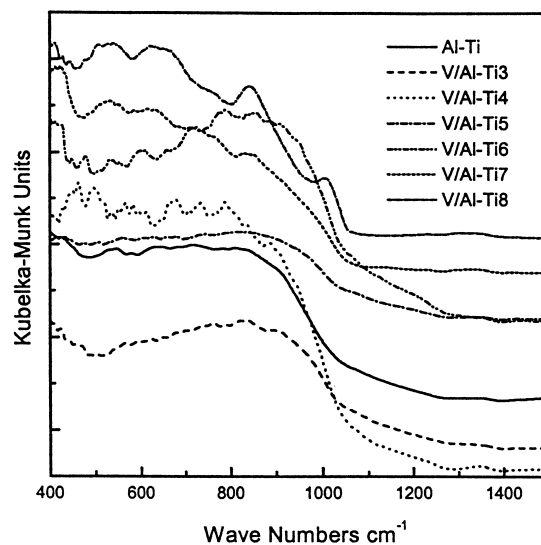


Fig. 7. DRIFT spectra of the catalysts evacuated at  $350^\circ\text{C}/30$  min (in the region  $400\text{--}2000\text{ cm}^{-1}$ ).

sponding to basic hydroxyl groups of alumina. In the sample V/Al-Ti 4 with a  $\text{V}_2\text{O}_5$  loading of 4.2 wt.%, the absence of this peak indicates the reaction of vanadia with basic hydroxyl groups of alumina. With further increase in vanadia loading the resonance at  $7.6$  ppm gradually decreased in intensity and in the samples V/Al-Ti 7 and 8 only a peak at  $5.5$  ppm could be seen corresponding to overlapping resonances from hydroxyl groups of vanadia, alumina and titania. Hydroxyl groups of vanadia were noticed at  $\sim 3.00$  ppm [16]. Pinaeva et al. [31] in their  $^1\text{H}$  NMR studies on  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts have noticed peaks at  $1.5$ ,  $2.3$ ,  $3.5$  ppm;  $5.6$ ,  $6.8$  and  $7.6$  ppm. The peak at  $6.4$  ppm was assigned to bridged OH groups and the peak at  $2.9$  ppm to terminal OH groups. They observed preferential reaction of  $\text{VOCl}_3$  with bridged OH groups (see also Table 3).

Diffuse reflectance FT-IR spectra of the catalysts and the support outgassed at  $350^\circ\text{C}$  are shown in Fig. 7. The vibrations corresponding to  $\text{V}=\text{O}$  were observed at  $\sim 1010\text{ cm}^{-1}$  only in the sample V/Al-Ti 8, and the corresponding overtones were observed at  $\sim 1900\text{--}2000\text{ cm}^{-1}$  in this sample. Due to the transparent nature of alumina support the observance of vibrations

Table 3  
 $^1\text{H}$  MAS NMR chemical shifts of the catalysts

Catalyst	$\delta_{\text{ppm}}$
V/Al-Ti 1	$-0.5, 2.9, 5.1, 7.5$
V/Al-Ti 2	$-0.4, 3.1, 5.3, 7.6$
V/Al-Ti 3	$-0.4, 3.2, 5.4, 7.6$
V/Al-Ti 4	$3.2, 5.6, 7.8$
V/Al-Ti 5	$2.9, 5.3, 7.7$
V/Al-Ti 6	$2.9, 5.3, 7.7$
V/Al-Ti 7	$5.4$
V/Al-Ti 8	$5.3$



corresponding to lower coordinated vanadia species is difficult in the skeletal vibration region.

#### 4. Conclusions

The present study shows that  $^{51}\text{V}$  solid-state NMR can be effectively employed to study the influence of pretreatment conditions on the molecular structure of vanadium oxide surface species in the catalysts. At lower vanadia loadings, highly dispersed monomeric tetrahedral vanadate species were observed and at higher  $\text{V}_2\text{O}_5$  loadings in the catalysts polymeric octahedrally coordinated vanadyl species were noticed.  $^1\text{H}$  MAS NMR studies indicate the preferential reaction of vanadia with the basic or terminal hydroxyl groups followed by the bridged or acidic hydroxyl groups. DRIFT studies of the catalysts showed the vibrations corresponding to polymeric vanadia species only at very high vanadia contents. The partial oxidation activity studies of the catalysts are in progress and the results would be helpful in determining the structure–activity relationships of the catalysts.

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