

APCAT A2365

## Physical and chemical characterization of surface vanadium oxide supported on titania: influence of the titania phase (anatase, rutile, brookite and B)

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(Received 31 March 1992, revised manuscript received 10 August 1992)

### Abstract

Different phases of titania were prepared and used to support ca. 1 wt.-%  $V_2O_5$ . The different titania phases prepared were: anatase (A22), rutile (R28), brookite (BT110) and B-phase (B18). Physical characterization of the various vanadia-titania catalysts was performed using X-ray photoelectron spectroscopy (XPS), in situ Raman and  $^{51}V$  solid state nuclear magnetic resonance (NMR) spectroscopy. The XPS results reveal that all the catalysts contain various levels of impurities. In situ dehydration Raman shows, for all the samples, the stretching vibration of the terminal  $V=O$  bond at ca.  $1030\text{ cm}^{-1}$ . Solid state  $^{51}V$  NMR spectra of all the samples in the dehydrated state show basically the same powder pattern with a peak maximum around  $-660$  to  $-670$  ppm. The combined Raman and NMR results indicate that the same surface vanadium oxide species is present on all the titania supports irrespective of the crystal structure of the bulk titania phase. Partial oxidation of methanol show similar activity and selectivity for the various vanadia-titania catalysts. The reaction selectivity was primarily to formaldehyde and methyl formate (92-96%). The turnover number for methanol oxidation was essentially the same for all the vanadia-titania catalysts and ranged from  $1.4$  to  $2.8\text{ s}^{-1}$ . These results indicate that the type of titania phase used as the support is not critical for partial oxidation over vanadia-titania catalysts as long as other parameters (e.g. surface impurities) are similar. Thus, the structure-reactivity

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studies of the different vanadia-titania catalysts suggest that the specific titania phase is not a critical parameter in determining the physical or chemical nature of the surface vanadia phase.

**Keywords:** anatase, B-phase, brookite, catalyst characterization (NMR, Raman spectroscopy, XPS), methanol oxidation, rutile, vanadia-titania

## INTRODUCTION

Many recent studies have shown that supported  $V_2O_5/TiO_2$  is a superior catalyst to unsupported crystalline  $V_2O_5$  for the selective oxidation of hydrocarbons, especially for the partial oxidation of *o*-xylene to phthalic anhydride [1-8]. Furthermore, many studies have suggested that the anatase phase of titania is the superior support for the selective partial oxidation reaction relative to the rutile phase. Recent studies have indicated also the possibility of using  $TiO_2$  B-phase as an effective support for the ammoxidation of toluene to benzonitrile with some success [9]. Early studies attributed the higher reactivity of the  $V_2O_5/TiO_2$  (anatase) catalyst to the ease of oxygen evolution under inert environments [10,11]. Vejux and Courtine [11] ascribed the higher reactivity of the  $V_2O_5/TiO_2$  (anatase) system to the crystallographic fit between the (010) plane of  $V_2O_5$  and the (010) or (001) plane of  $TiO_2$  (anatase). Likewise, the lower activity of  $V_2O_5/TiO_2$  (rutile) was attributed to the misfit of the lattice parameters of the two corresponding bulk phases. Since then these conclusions have been strongly disputed with the discovery of a two-dimensional vanadium oxide overlayer on the  $TiO_2$  support [3,8,12]. This overlayer is neither in epitaxial registry with the support nor does it have a structure corresponding to that of bulk  $V_2O_5$ .

Gasior et al. [5,13] concluded from comparative studies with  $V_2O_5$  supported on  $TiO_2$  (anatase) and  $TiO_2$  (rutile) that the surface vanadium oxide species is not stable on  $TiO_2$  (rutile) and, consequently, exhibits inferior catalytic properties. Van Hengstum et al. [14] studied the effect of  $TiO_2$  (anatase and rutile) interactions with  $V_2O_5$  through the gas-phase oxidation of toluene and methanol. These authors concluded that the difference between  $V_2O_5/TiO_2$  (anatase) and  $V_2O_5/TiO_2$  (rutile) is largely due to the difference in crystal structure rather than surface accumulation of silica and alumina which was detected by X-ray photoelectron spectroscopy (XPS). Machej et al. [15] found that there was a difference in the catalytic behavior of  $V_2O_5/TiO_2$  (anatase) and  $V_2O_5/TiO_2$  (rutile) for the dehydration of *N*-ethylformamide. The difference in catalytic activity was attributed to the difference in the type of reduced vanadia phases formed on the different titania phases (anatase and rutile).

In contrast, Murakami and co-workers [16-19] did not find any difference between a series of  $V_2O_5/TiO_2$  (anatase),  $V_2O_5/TiO_2$  (rutile) and  $V_2O_5/TiO_2$  (anatase + rutile) catalysts using in situ IR during ammonia adsorption, the

rectangular pulse technique which measures the nitrogen concentration profile produced after the adsorption of nitric oxide and ammonia, benzaldehyde–ammonia titration (BAT), and other physical characterization techniques as well as the selective catalytic reduction of nitric oxide using ammonia. Cavani et al. [20] found that the crystalline structure of  $\text{TiO}_2$  did not influence the activity of the catalysts in the ammoxidation of toluene and oxidation of *o*-xylene. Slinkard and DeGroot [21] found that supported  $\text{V}_2\text{O}_5/\text{TiO}_2$  (rutile) is more selective for the oxidation of *n*-butenes to acetic acid and acetaldehyde than supported  $\text{V}_2\text{O}_5/\text{TiO}_2$  (anatase). Cai and Ozkan [22], using the selective catalytic reduction of nitric oxide reaction, found that the activity of  $\text{V}_2\text{O}_5/\text{TiO}_2$  (anatase) and  $\text{V}_2\text{O}_5/\text{TiO}_2$  (rutile) were similar although  $\text{V}_2\text{O}_5/\text{TiO}_2$  (rutile) was more active than  $\text{V}_2\text{O}_5/\text{TiO}_2$  (anatase) on a unit surface area basis.

Saleh et al. [23] employed Raman spectroscopy to examine the nature of the supported vanadium oxide species on  $\text{TiO}_2$  (anatase) and  $\text{TiO}_2$  (rutile). The Raman studies showed that under ambient conditions the surface vanadium oxide Raman bands on  $\text{TiO}_2$  (anatase) were broader than on  $\text{TiO}_2$  (rutile). No mention of the surface contamination was provided, however, more recently XPS surface analysis showed that the surface anatase sample contained potassium and phosphorus and the rutile sample contained silica [24]. Using solid state  $^{51}\text{V}$  nuclear magnetic resonance (NMR), Eckert et al. [24] showed that under ambient conditions the surface vanadium oxide species is predominately in octahedral coordination, irrespective of the titania phase used. However, the coordination environment of vanadia is markedly influenced by the presence of impurities and loading on the surface of the titania support. Recent studies have demonstrated that under ambient conditions the surface of oxide supports is hydrated and that the surface vanadium oxide structure is governed by the net pH at point of zero charge of the surface [25]. Furthermore, upon removal of the hydration sphere on the surface, under dehydration conditions, the surface vanadium oxide transforms and the structure present under ambient conditions is lost. Even though several recent studies deal with the structure of the surface vanadium oxide species under dehydrated conditions [26–36], a detailed characterization study has not been carried out to address the effect of the different phases of the titania support on the physical and chemical properties of the vanadia–titania system.

One of the major complications arising from the comparative analysis of the  $\text{V}_2\text{O}_5/\text{TiO}_2$  (anatase) and the  $\text{V}_2\text{O}_5/\text{TiO}_2$  (rutile) catalysts is the origin and nature of the titania supports. The titania supports used in most of these studies were primarily obtained from pigment manufacturers. Due to intentional introduction, or as a result of manufacturing procedures, a variety of additives/impurities such as K, P, Cl, Al or Si are known to exist on the titania surface [5,6,24]. Due to the presence of the impurities it was difficult to isolate the origin of differences, if any, of the different titania phases. Thus, in order to elucidate the influence of the titania phase and to gain a fundamental under-

standing of the  $V_2O_5/TiO_2$  system, it is critical that detailed physical and chemical characterization studies be performed with these catalysts.

The present study focuses on the influence of the different titania phases on the structure and reactivity of the surface vanadia species for the  $V_2O_5/TiO_2$  system. Anatase and rutile are prepared from the same starting material,  $TiCl_4$ , with an objective to eliminate the possibility of having different levels of impurity due to different precursors or different manufacturing procedures. High surface area brookite, prepared from titanium isopropoxide; B-phase titania, prepared using the prescribed procedure [37]; and commercially available  $TiO_2$  (Degussa P-25), are also used as support materials. The physical nature of the titania surface after depositing the vanadium oxide overlayer is first checked for surface contamination by XPS. The surface vanadium oxide structure is studied with Raman spectroscopy and solid state  $^{51}V$  NMR under in situ dehydrated conditions. The chemical nature of the surface vanadium oxide species is probed using the partial oxidation of methanol. The results from the physical (XPS, Raman, NMR) and chemical (methanol oxidation) characterization studies are combined which allowed definite conclusions to be made regarding the effect of the titania support phase on the nature of the surface vanadium oxide species.

## EXPERIMENTAL

### *Preparation of titania*

(1) Two  $TiO_2$  samples were prepared by the hydrolysis of  $TiCl_4$ . For the anatase preparation,  $TiCl_4$  was added to distilled water. This was followed by filtering, washing, drying at  $120^\circ C$  and finally calcining at  $500^\circ C$  for 1 h. The resulting solid was pure anatase (checked by Raman) with a surface area of  $22\text{ m}^2/\text{g}$  and was denoted as A22. The  $TiO_2$  rutile phase was also prepared from  $TiCl_4$ . To prepare the rutile phase,  $TiCl_4$  was partially hydrolyzed in an aqueous HCl solution. The final pH of the resulting solution was  $< 1.0$ . Precipitation was carried out by heating the solution at  $70\text{--}80^\circ C$ . The resulting solid was dried at  $120^\circ C$  and finally calcined at  $500^\circ C$  for 1 h. The sample showed only traces of the anatase features in the Raman spectrum. The surface area of this sample was  $28\text{ m}^2/\text{g}$  and was denoted as R28.

(2) Titania was also obtained by the hydrolysis of titanium isopropoxide oxide. Titanium isopropoxide oxide (Aldrich) was gradually added to a beaker of water. The final ratio of titanium isopropoxide to water was 1:7.5. The entire preparation and room temperature drying for 16 h was performed under a nitrogen atmosphere. This was followed by drying at  $110^\circ C$  in oxygen for 16 h followed by calcination at  $400^\circ C$  for 2 h. The resulting titania produced had a surface area of  $110\text{ m}^2/\text{g}$  and was found via X-ray diffraction to consist of the brookite phase of titania as a major component ( $> 50\%$ ). The anatase phase

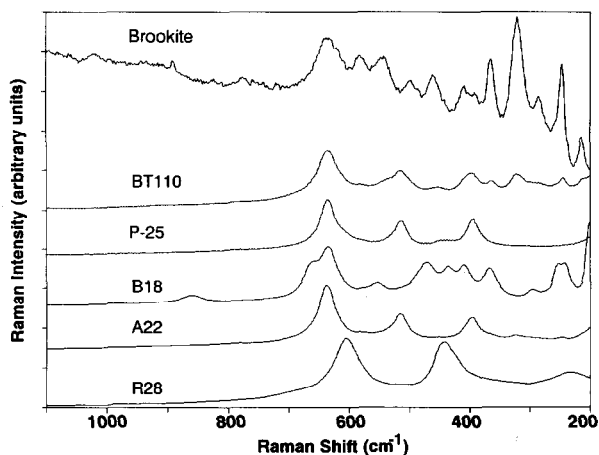


Fig. 1. Raman spectra of the different titania supports and the brookite phase of titania.

of titania was also detected by Raman spectroscopy as well as X-ray diffraction and makes up the balance. Representative Raman bands due to the brookite phase of titania at 242, 320 and 363  $\text{cm}^{-1}$  are also observed for this titania sample (see Fig. 1). This sample was denoted as BT110.

(3) The B-phase of  $\text{TiO}_2$  was prepared from the tetratitanate ( $\text{K}_2\text{Ti}_4\text{O}_9$ ). Complete hydrolysis corresponding to complete extraction of potassium from the tetratitanate was achieved by  $\text{HNO}_3$  solution for three days. This was followed by filtration and vacuum drying at room temperature and finally calcining the product at 500°C. Details of the preparation procedure can be found elsewhere [37]. This sample was denoted as B18.

(4) Commercially available  $\text{TiO}_2$ , Degussa P-25 (surface area 50  $\text{m}^2/\text{g}$ ; anatase/rutile ratio ca. 2) was also used as a support. This sample was denoted as P-25.

#### *Preparation of vanadia-titania samples*

Low loadings of  $\text{V}_2\text{O}_5$  (ca. 1 wt.-%) were prepared on all of the above mentioned titania supports. On A22 and R28, vanadia was deposited by the aqueous impregnation with vanadium oxalate followed by drying at 120°C for 16 h and calcining in air at 450°C for 2 h. On BT110 and B18 low loadings of vanadia were prepared by the incipient wetness impregnation of  $\text{VO}(\text{OC}_3\text{H}_7)_3$  in methanol under a nitrogen atmosphere. The samples were dried at room temperature for 16 h followed by drying at 110°C for 16 h in a nitrogen atmosphere. The final calcination was performed at 400°C in dry air. On Degussa P-25 low loadings of vanadia were prepared by the incipient wetness impregnation with  $\text{VO}(\text{OC}_2\text{H}_5)_3$  in ethanol and subsequent drying at 120°C for 16 h, all done

TABLE 1

Surface area of bulk titania and amount of vanadia deposited on vanadia-titania samples

Titania support	Surface area of bulk titania (m <sup>2</sup> /g)	Amount of deposited V <sub>2</sub> O <sub>5</sub> (wt.-%)
P-25	50	1.02
R28	28	1.02
A22	22	0.95
BT110	110	1.02
B18	18	0.89

under a nitrogen atmosphere. The samples were finally calcined in air at 450°C for 2 h. The final vanadium oxide contents were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis. Surface area and amount of vanadium oxide deposited on the different titania phases are listed in Table 1. As shown previously, the preparation method does not influence the surface vanadia phase on different titania supports [38].

### Raman

The in situ Raman spectra of the different vanadia-titania samples were obtained with a Spectra-Physics Ar<sup>+</sup> laser (Model 171) by utilizing about 30-50 mW of the 514.5 nm line for excitation. Each sample containing about 250 mg of pure catalyst was pressed into a 2 mm thin pellet and mounted onto a stationary sample holder that was installed in an in situ cell. Both the sample holder and cell were made of quartz. Oxygen (Linde Ultra High Purity) was passed through the cell at a rate of 100-200 sccm. The laser irradiation scattered by the sample was directed into a Spex Triplemate Spectrometer (Model 1877). The scattered light after being filtered was focussed on the photodiode array and were scanned with an optical multichannel analyzer (OMAIII: EG&G, Princeton Applied Research, Model 1463). The combination of a detector containing ca. 700 intensified pixel elements and a grating of 1800 grooves/mm in the spectrograph stage provided a higher resolution of the recorded spectra (experimentally determined to be better than 1 cm<sup>-1</sup>). Three spectra were recorded for each sample: at room temperature under ambient air, in flowing dry oxygen at 450°C, and near room temperature (50°C) after cooling in flowing dry oxygen to eliminate thermal broadening. The Raman bands of the dehydrated samples near room temperature (50°C) are reported in this paper. Additional details on the in situ cell and Raman set up can be found elsewhere [38].

### *Solid state $^{51}\text{V}$ nuclear magnetic resonance*

Room temperature solid state  $^{51}\text{V}$  NMR studies were carried out at a field strength of 7.05 T (resonance frequency 79.0 MHz), using a General Electric GN-300 NMR spectrometer equipped with an Explorer fast digitizer and a probe from Doty Scientific. The spectra were acquired with a  $10^\circ$  pulse of  $1\ \mu\text{s}$  length and 1 s relaxation delays. For studies under in-situ conditions, the samples were heated for 2 h in a  $10^{-3}$  Torr (1 Torr = 133.3 Pa) vacuum at  $300^\circ\text{C}$ , subsequently reoxidized in an oxygen atmosphere at the same temperature, and then flame sealed at room temperature under vacuum into 5 mm ampules.

### *X-ray photoelectron spectroscopy*

The X-ray photoelectron spectroscopy (XPS) analysis of the various vanadia-titania catalysts were obtained using an X-ray beam of predominantly Mg  $K\alpha$  or Al  $K\alpha$  X-rays. Specimens for the XPS analysis were prepared by pressing the catalyst powders between a stainless steel holder and a polished single crystal silicon wafer. The samples were transferred to a turbomolecular pumped airlock evacuated at ca.  $1 \times 10^{-7}$  Torr. The samples were then installed in the vacuum chamber of a Model DS800 XPS surface analysis system manufactured by Kratos Analytical Plc., Manchester, UK. The chamber was evacuated to a base pressure of ca.  $1 \times 10^{-9}$  Torr. A hemispherical electron energy analyzer was used for electron detection.

### *Methanol oxidation*

Methanol oxidation reactions were carried out using a mixture of  $\text{CH}_3\text{OH}/\text{O}_2/\text{He}$  in the molar ratio of ca. 6/11/83 as the reactant gas. A  $\text{O}_2/\text{He}$  mixture obtained from two mass flow controllers (Brooks) was bubbled through a flask containing methanol and the outlet gas was passed through a condenser operating at  $9.5\text{--}9.6^\circ\text{C}$  to obtain the required  $\text{CH}_3\text{OH}$  molar ratio in the gas phase. The gas flow-rate was maintained at ca. 100 sccm for all the catalytic runs in order to keep the conversions low ( $< 8\ \text{mol}\%$ ). Analysis of the products were performed on an on-line gas chromatograph (GC) using two thermoconductivity detectors (TCD) and a flame ionization detector (FID) with two packed columns (Poropak R and Carbosieve SII). Three to five sets of data were obtained for milligram amounts of all the vanadia-titania catalysts and the average initial turnover number (TON) was obtained along with the standard deviation ( $\sigma$ , presented in the data as the error). The TON ( $\text{s}^{-1}$ ) was calculated from the moles of methanol converted per mole vanadium atom per second. The TON was calculated using the conversion obtained after 10-20 min of reaction. The conversions of the various vanadia-titania catalysts did not vary more than ca. 10% with time. Reaction data were collected for 8-10 h.

## RESULTS

The XPS surface analysis of the various vanadia-titania catalysts, Table 2, reveal that all the surfaces are contaminated with some sort of impurity. The impurity levels in Table 2 are normalized with respect to the titanium atomic concentration in the sample to eliminate the effect of the carbon signal. The vanadium oxide supported on P-25 is contaminated with chlorine (0.29 at.-%) and silicon (0.75 at.-%). Vanadium oxide supported on BT110 is contaminated with chlorine (0.37 at.-%) and fluorine (0.23 at.-%). Vanadium oxide supported on A22 and R28 is contaminated with sodium (0.3 and 0.18 at.-%, respectively), chlorine (0.16 and 0.27 at.-%, respectively) and silicon (0.48 and 2.3 at.-%, respectively). Vanadium oxide supported on B18 is contaminated with phosphorus (1.5 at.-%).

Raman spectroscopy is sensitive to metal-oxygen vibrations which are related to the M-O bond (M=metal, O=oxygen) lengths and structures, and the metal-oxygen vibrations usually lie in the 100-1200  $\text{cm}^{-1}$  region [39]. Only metal-oxygen vibrations due to the surface vanadia species in the 800-1200  $\text{cm}^{-1}$  region are reported since the different titania phases are Raman active in the 100-800  $\text{cm}^{-1}$  region as observed from Fig. 1. For this reason only the relevant vanadium-oxygen vibration in the 800-1200  $\text{cm}^{-1}$  region are presented in Table 3. The in situ dehydration Raman spectroscopy studies of the various vanadia-titania catalysts reveal a Raman band at ca. 1030  $\text{cm}^{-1}$  characteristic of a vanadium-oxygen terminal double bond [39]. Vanadia supported on BT110, which has the highest surface area of the different titania supports, possesses a Raman band at 1025  $\text{cm}^{-1}$ . Vanadia supported on B18, which has the lowest surface area of the different titania supports, and R28 possesses a Raman band at 1031  $\text{cm}^{-1}$ , whereas vanadia supported on P-25 and A22 possesses a Raman band at 1028  $\text{cm}^{-1}$ . Solid state  $^{51}\text{V}$  NMR is sensitive to the coordination environment of the vanadium nucleus [26,27]. It is able to distinguish between different four- and six-coordinated vanadium (V)

TABLE 2

Surface analysis of the various vanadia-titania catalysts by XPS

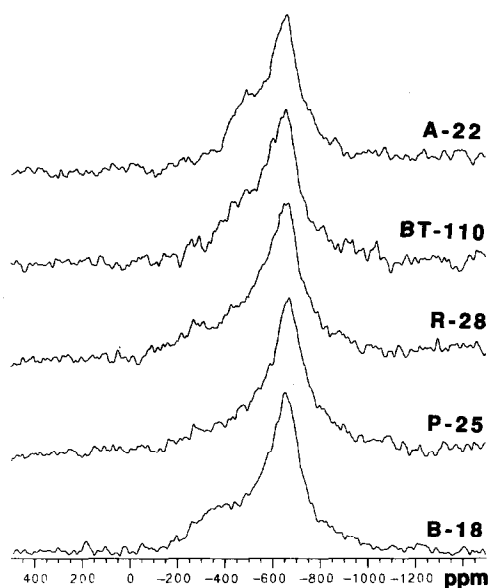
Ca. 1% $\text{V}_2\text{O}_5$ on titania support	Surface atomic ratio of element to titanium					
	V	Na	Cl	F	Si	P
P-25	0.010	0.00	0.01	0.00	0.03	0.00
R28	0.039	<0.01	0.01	0.00	0.10	0.00
A22	0.010	0.01	<0.01	0.00	0.02	0.00
BT110	0.014	0.00	0.02	0.01	0.00	0.00
B18	0.069	0.00	0.00	0.00	0.00	0.07



TABLE 3

Dehydrated Raman band of the surface vanadia species in the vanadia-titania catalysts

Ca. 1% V <sub>2</sub> O <sub>5</sub> on titania support	Raman shift (cm <sup>-1</sup> )
P-25	1028
R28	1031
A22	1028
BT110	1025
B18	1031

Fig. 2. Dehydrated solid-state <sup>51</sup>V NMR spectra of the different vanadia-titania catalysts.

oxide species. Irrespective of the titania phase used as the support, the dehydrated solid state <sup>51</sup>V NMR studies of the various vanadia-titania catalysts in Fig. 2, reveal more or less identical powder patterns with a peak maximum around -660 to -670 ppm. This is characteristic of vanadia in low coordination [26,27]. Thus, in situ Raman and <sup>51</sup>V NMR studies reveal that the same surface vanadia species is present on all the different titania supports under dehydration conditions.

The methanol oxidation reaction was carried out for the various vanadia-titania catalysts and the results are presented in Table 4. The activity of the vanadia-titania catalysts were normalized per vanadium atom to calculate the TON. The main product of methanol oxidation over the various vanadia-ti-

TABLE 4

Methanol oxidation reaction for the various vanadia-titania catalysts

Ca. 1% V <sub>2</sub> O <sub>5</sub> on titania support	TON <sup>a</sup> (s <sup>-1</sup> )	Selectivity to HCHO and HCOOCH <sub>3</sub> (%)
P-25	1.9 ± 0.2	96
R28	2.8 ± 0.4	96
A22	2.3 ± 0.2	92
BT110	1.4 ± 0.1	96
B18	2.0 ± 0.1	96

<sup>a</sup> Based on amount of vanadia actually deposited (see Table 1).

tania catalysts is formaldehyde and methyl formate (combined selectivity >92%). The TON's of the various vanadia-titania catalysts differ by a factor of two. The highest TON is obtained for vanadium oxide supported on TiO<sub>2</sub> (R28) (2.8 s<sup>-1</sup>) and lowest TON is obtained for vanadium oxide supported on TiO<sub>2</sub> (BT110) (1.4 s<sup>-1</sup>). The TON of the remaining vanadia-titania catalysts have intermediate values. The TON's of the vanadia supported on A22 and R28 are very similar (2.3 and 2.8 s<sup>-1</sup>, respectively), while the TON for the vanadium oxide supported on P-25 and B-phase samples are 1.9 and 2.0 s<sup>-1</sup>, respectively. The selectivity of the various vanadia-titania samples are 96% towards HCHO and HCOOCH<sub>3</sub>, except for vanadia supported on A22 where the selectivity drops to 92%. For vanadia supported on TiO<sub>2</sub> (A22) an increase in the selectivity towards CO/CO<sub>2</sub> (ca. 4%) is observed. The balance for all the supported vanadia-titania catalysts is made up of dimethyl ether and dimethoxymethane (ca. 2% each). The amount of dimethyl ether, a product from the pure titania support, corresponds well with the weight of sample used for the methanol oxidation reaction. Thus, the specific activity and selectivity of the different vanadia-titania catalysts for methanol oxidation are very similar.

## DISCUSSION

Traditionally most surface characterization studies of supported vanadium oxide catalysts were performed under ambient conditions. Recently, it was observed that under ambient conditions the surface of the catalysts adsorbed moisture which governed the molecular structure of the surface vanadium oxide species [25-27]. However, under reaction temperatures (200-500°C) the moisture desorbs from the surface resulting in a dehydrated environment for the surface vanadium oxide species [36]. As a result of dehydration, the surface vanadium oxide species directly bonds to the oxide support via V-O-support bonds (V=vanadium; O=oxygen) and also forms terminal V=O bonds.

The presence of the terminal V=O bond has been identified by vibrational spectroscopy. This is in contrast to the hydrated surface vanadium oxide species, which is essentially in a solvated state on the oxide support surface under ambient conditions [25-27]. These observations of hydration and dehydration of the oxide surface makes it imperative that the correlation of the structure-reactivity data should be performed with the structural data obtained under dehydrated conditions, and then relating this structural information with the reactivity data.

The present study shows that under in situ dehydrated conditions, irrespective of the phase of titania used, the Raman band for the terminal vanadium-oxygen bond occurs at 1025-1031  $\text{cm}^{-1}$ . The slight shift of the Raman band for the vanadium-oxygen double bond from 1025  $\text{cm}^{-1}$  to 1031  $\text{cm}^{-1}$  can be related to the surface concentration of the vanadium oxide species. Similar shifts are observed as a function of coverage for vanadia supported on  $\text{TiO}_2$  (P-25) where the Raman band of the V=O stretching vibration changed from 1027 to 1031  $\text{cm}^{-1}$  as the vanadium oxide loading is increased from 1%  $\text{V}_2\text{O}_5$  to 5%  $\text{V}_2\text{O}_5$  [28]. In addition to the in-situ Raman studies, previous in-situ Fourier transform-infrared (FT-IR) studies of the vanadia-titania catalysts indicate an absorbance at 1035  $\text{cm}^{-1}$  [30,31,35]. Using group theory, this close correspondence of the vanadium oxygen stretching frequencies in the Raman and IR measurements indicate the presence of a single vanadium oxygen terminal bond (V=O) [30]. Mono-oxo vanadium oxide (V=O) species are also substantiated by  $^{18}\text{O}$ - $^{16}\text{O}$  exchange experiments [31].

The dehydrated solid state  $^{51}\text{V}$  NMR spectra of vanadium oxide supported on the different titania phases shows that the surface vanadium oxide phase, at low loadings, possesses an intensity maximum in wideline NMR spectra at -660 to -670 ppm. This indicates the presence of essentially the same vanadium environment for the surface vanadium oxide species on the different titania phases. The low value for the chemical shift in the wideline NMR is characteristic of vanadium (oxide) in low coordination based on the wideline NMR spectra of various known vanadium(V) oxide containing compounds [26,27]. Similar chemical shifts for dehydrated surface vanadium oxide species were previously observed on titania (anatase, 80  $\text{m}^2/\text{g}$ ) and alumina, and were assigned to a distorted tetrahedral vanadium oxide surface species [26,27].

The various vanadia-titania catalysts have different amounts of impurities present as detected by XPS (see Table 2). The XPS technique inherently detects the first 10-40 Å of the surface region. Therefore, it is not known whether these impurities are indeed associated with the outer titania surface layer where the vanadium oxide overlayer is located. In order to clarify the effect of impurities, various impurities were intentionally added to 1%  $\text{V}_2\text{O}_5/\text{TiO}_2$  (P-25) [40,41]. It was observed that low levels of non-interacting metal oxide impurities (tungsten, niobium, and silicon) did not dramatically affect the structure of the surface vanadium oxide species and only a slight shift of the Raman

band due to the terminal V=O bond was observed. However, small amounts of basic metal oxide impurities (potassium) significantly shifted the Raman band of the terminal V=O bond to lower wavenumbers. The addition of presence of low levels of phosphorus in the parent titania broadens the Raman band due to the terminal V=O bond. Thus, from the above information the presence of high amounts of sodium on TiO<sub>2</sub> (A22) (see Table 2; V:Na ≈ 1), should decrease the Raman band due to the terminal V=O bond. Indeed the Raman band for ca. 1% V<sub>2</sub>O<sub>5</sub> on TiO<sub>2</sub> (A22) is shifted from 1031 (expected) to 1028 cm<sup>-1</sup>. The amount of sodium present in the vanadia on TiO<sub>2</sub> (R28) catalyst is evidently too small to affect the Raman band of the terminal V=O bond (see Table 2; V:Na > 4). The presence of silica on the various vanadia-titania catalysts does not affect the Raman band for the terminal V=O bond and no unexplainable shift in the various vanadia-titania catalysts is observed (to be confirmed). The presence of low levels of phosphorus in B18, as stated earlier, does not affect the position of the Raman band of the terminal V=O bond. The level of surface chlorine and fluorine decreases with an increase in vanadia loading on P-25. The shift in the Raman band of the terminal V=O bond, however, is associated with the increase in loading rather than the decrease in the amount of halides present. Hence, the chlorine and fluorine present in P-25 and BT110 do not affect the Raman band of the terminal V=O bond. Thus, the presence of small amounts of basic impurities (e.g. sodium, potassium, etc.) on the titania surface can critically influence the nature of the surface vanadium oxide structure and care must be taken to detect the presence of such impurities before performing further analysis.

Hence, the combined Raman and <sup>51</sup>V NMR dehydration studies, along with the XPS data, and knowledge of certain model doped vanadia-titania catalysts indicate that at low loadings the surface vanadium oxide species on the different titania support phase (anatase, rutile, brookite or B) are similar. The surface vanadium oxide species possesses one terminal bond, and has a low coordination number with respect to oxygen. In addition, small amounts of vanadia coordinated with sodium may be present for the vanadia supported on TiO<sub>2</sub> (A22) catalyst. An idealized representation of the surface vanadium oxide species on the different titania phases is given in Fig. 3.

A similar model of the surface vanadium oxide phase has been proposed before for vanadia supported on various other oxide supports (SiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>,

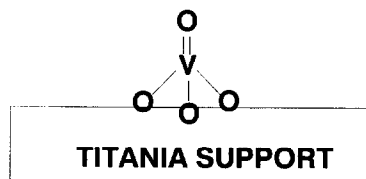


Fig. 3. Structure of the surface vanadia phase on the different vanadia-titania catalysts.

$\text{Al}_2\text{O}_3$ , and  $\text{ZrO}_2$ ) despite the wide range of properties [26–29,32–34]. In comparison to the different oxide supports, the similarity of surface vanadium oxide phases on the different titania phases in the present study is trivial but a necessary and important conclusion for analysis of structure–reactivity relationship. Without a similarity in structure it is difficult to assign unambiguously any similarity or differences in the reactivity of the vanadia–titania catalysts to the titania support phase or surface vanadium oxide structure.

The methanol oxidation reaction was used to probe chemically the activity and selectivity of the vanadia–titania catalysts. The oxidation of methanol is very sensitive towards the presence of surface acid or surface redox sites. The presence of surface acid sites, for example on bulk  $\text{Al}_2\text{O}_3$  or bulk  $\text{TiO}_2$ , produces dimethyl ether. The presence of surface redox sites produces partial oxidation products: formaldehyde, methyl formate, and dimethoxymethane. Total oxidation of methanol produces carbon monoxide and carbon dioxide and surface basic sites also appear to produce carbon monoxide and carbon dioxide [40,41]. Previous investigations have shown that the turnover number towards the selective oxidation of methanol to formaldehyde varies over three orders of magnitude upon the addition of low loadings (1 wt.-%  $\text{V}_2\text{O}_5$ ) of vanadia to various oxide supports ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{TiO}_2$ ) [33]. Therefore, the formation of redox sites, due to the addition of vanadia on various oxide supports is readily detected by studying the methanol oxidation activity, and the partial oxidation of methanol is a very sensitive chemical probe to study the redox activity of the surface vanadium oxide species.

The activity of the  $\text{TiO}_2$  support, per gram of the sample, is two orders of magnitude less than the activity of the vanadia–titania catalysts. Furthermore, the primary product of the  $\text{TiO}_2$  support is dimethyl ether. The trace amounts of dimethyl ether produced during the methanol oxidation reaction can be attributed to the exposed  $\text{TiO}_2$  support. In essence, the activity of the various vanadia–titania catalysts primarily originates from the surface vanadium oxide species which form the redox sites. The presence of redox sites in the various supported vanadia–titania catalysts is evident as formaldehyde and methyl formate (methyl formate is the minor product: selectivity, which depends upon conversion, < 4%) are the primary products ( $\geq 92\%$ ). The similarity in selectivity, in addition to the similarity in structural characterization already discussed, provides a basis for comparison of the various supported vanadia–titania catalysts.

The primary observation in the activity of the various vanadia supported on titania catalysts is the extremely close correspondence of the TON and selectivity. The vanadium oxide supported on  $\text{TiO}_2$  (R28) has the highest TON and it is two times the TON for the lowest vanadia–titania sample (BT110). This can be compared to the various supported vanadium oxide catalysts, where the TON was found to decrease by three orders of magnitude when the support was changed from  $\text{TiO}_2$  and  $\text{ZrO}_2$  to  $\text{SiO}_2$ , and the  $\text{V}_2\text{O}_5/\text{TiO}_2$  (P-25) catalysts,

where the TON varies between 1.1 to 2.7 s<sup>-1</sup> as the vanadium oxide loading is changed from 1 to 6% V<sub>2</sub>O<sub>5</sub> [41]. Thus, the factor of two for the variation in TON for the supported vanadia-titania catalysts is not kinetically significant. All of the vanadia-titania samples show a high selectivity towards partial oxidation products. The slight decrease in the selectivity of vanadia supported on TiO<sub>2</sub> (A22) towards formaldehyde and methyl formate (92%) with a corresponding increase in the formation of CO/CO<sub>2</sub> is attributed to the large amounts of sodium present in the sample (see Table 2: atomic V/Na ratio ca. 1). Parallel studies of potassium promoted vanadium oxide supported on P-25, also show a similar trend [40,41]. Addition of potassium to 1% vanadia supported on P-25 shows a decrease in total activity and an increase in selectivity towards CO/CO<sub>2</sub>.

Comparison of Tables 3 and 4 indicates that there is no correspondence between the position of the Raman band of the terminal V=O bond and the turnover number. Similar conclusions were observed while studying methanol oxidation on different oxide supports [33]. The position of the Raman band is related to the bond strength of the vibrating diatomic (vanadium and oxygen) species [39]. A stronger bond strength implies a shift of the Raman band to higher wavenumbers. However, since no relationship is observed between the position of the Raman band for the terminal V=O bond and the TON, the activity is not related to the strength of the terminal V=O bond. This is contrary to previous studies, which proposed that the strength of the V=O terminal bond controls the activity for partial oxidation [42].

In retrospect, the partial oxidation reaction has been related to the reducibility of the supported metal oxide catalysts, which in turn is related to the bridging M-O-S (M=supported metal, O=oxygen, and S=support) bond [33]. Thus, it would be expected that the different titania phases should be essentially equal. This conclusion is possible if the structure of the supported metal oxide is the same. The present study clearly shows that the structure of the various vanadia-titania catalysts are similar, and, indeed, so are the activities.

## CONCLUSIONS

A series of titania samples were prepared and used for supporting the surface vanadia species. Physical characterization was carried out using XPS, Raman, and solid state <sup>51</sup>V NMR. Chemical characterization was performed using the methanol oxidation reaction.

Much effort was devoted to the synthesis of the pure anatase, rutile, and B phase, but it was difficult to obtain a titania surface completely devoid of impurities. However, within the slight variations in surface impurities, it is clear that at these loadings there is practically no physical or chemical difference between the vanadia supported on various titania supports, and that the ti-

tania phase (anatase, rutile, brookite, B-phase, or A + R) does not influence the physical and chemical characteristics of the active surface vanadia species.

#### ACKNOWLEDGEMENTS

The authors would like to thank J. Johnson for providing the B-Phase of titania, Dr N. Spencer for analyzing the vanadia content of the samples, and Dr. E. Sabino for obtaining the X-ray diffraction patterns of the titania supports. Financial support of NSF Grant No. CTS-9006258, NSF Program No. INT-8822945, and the Polish Academy of Sciences for this international cooperative science program is gratefully acknowledged.

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