

## Partial Oxidation of Ethane over Monolayers of Vanadium Oxide. Effect of the Support and Surface Coverage.

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The nature of supported oxides and of the support plays a critical role in the partial oxidation of hydrocarbons since the support is not only providing a high surface area, but also dispersing the oxide. The interaction between the metal oxide overlayer and the underlying support similarly determines the performance of the catalyst, which may also be affected by the exposed sites of the support. To fully understand these effects, a series of supported vanadium oxide catalysts at monolayer and submonolayer coverage have been prepared. The monolayer coverage was determined by Raman spectroscopy and X-ray photoelectron spectroscopy. The activity of the supported vanadium oxide catalysts is determined by the specific support and surface vanadia coverage.

### 1. INTRODUCTION

Supported metal oxides are currently being used in a large number of industrial applications. The oxidation of alkanes is a very interesting field, however, only until recently very little attention has been paid to the oxidation of ethane, the second most abundant paraffin (1). The production of ethylene or acetaldehyde from this feed stock is a challenging option. Vanadium oxide is an important element in the formulation of catalysts for selective catalytic reactions (e. g. oxidation of o-xylene, 1-3, butadiene, methanol, CO, ammoxidation of hydrocarbons, selective catalytic reduction of NO and the partial oxidation of methane) (2-4). Many of the reactions involving vanadium oxide focus on the selective oxidation of hydrocarbons, and some studies have also examined the oxidation of ethane over vanadium oxide based catalysts (5-7) or reviewed the activity of vanadium oxide for the oxidation of lower alkanes (1). Our work focuses on determining the relevance of the specific oxide support and of the surface vanadia coverage on the nature and activity of the supported vanadia species for the oxidation of ethane.

## 2. EXPERIMENTAL

### 2.1. Synthesis

The oxide supports employed in the present study were: SiO<sub>2</sub> (Cabot), Al<sub>2</sub>O<sub>3</sub> (Engelhard), CeO<sub>2</sub> (Engelhard), TiO<sub>2</sub> (Degussa), ZrO<sub>2</sub> (Degussa), and Nb<sub>2</sub>O<sub>5</sub> (Niobium Products Co.). All supports were pretreated at 773 K overnight. The silica support was also treated with water vapor, this support will be referred to as SiO<sub>2</sub>-H<sub>2</sub>O. The catalysts were prepared by incipient wetness impregnation with V-isopropanol in a glove box with nitrogen flow. The impregnated samples were kept at room temperature overnight in the glove box. Then, the samples were dried at 393 K for 1 h and at 573 K another 1 h with nitrogen flow. Finally, the samples were calcined at 573 K for 1 h and 723 K for 2 h in flowing oxygen. The catalysts were prepared with several vanadium oxide loading ranging from very low surface vanadium coverage to the presence of crystalline V<sub>2</sub>O<sub>5</sub>. The catalysts are referred to as "xVS", where "x" represents the weight percent of V<sub>2</sub>O<sub>5</sub> and "S" stands for the element of the specific oxide support.

### 2.2. Characterization

The *vanadium content* in the catalysts was determined with a Perkin-Elmer Mod. 3030 Atomic Absorption Spectrometer. The *surface areas* of the catalysts and of the corresponding supports were determined by nitrogen adsorption/desorption isotherms on a Micromeritics Mod. 2000 ASAP.

*X Ray photoelectron (XPS) spectra* were acquired with a Fisons ESCALAB 200R electron spectrometer equipped with a hemispherical electron analyzer and an MgK $\alpha$  X-ray source ( $h\nu = 1253.6$  eV) powered at 120 watts. A PDP 11/05 computer from DEC was used for collecting and analyzing the spectra. The samples were placed in small copper cylinders and mounted in a transfer rod placed in the pretreatment chamber of the instrument. The base pressure in the ion-pumped analysis chamber was maintained below  $5 \times 10^{-9}$  Torr during data acquisition. The spectra were collected for 30 to 100 min at a pass energy of 10 eV ( $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ ), which is typical of high resolution conditions. The intensities were estimated by calculating the integral of each peak after smoothing and subtraction of the "S-shaped" background and fitting the experimental curve to a combination of Gaussian and Lorentzian distributions, the G/L proportion of which varied in the range 5-27%. All binding energies (BE) were referenced to the support cation, giving values with an accuracy of  $\pm 0.2$  eV.

The molecular structures of the surface vanadium oxide species on the different supports were examined with *Raman spectroscopy*. The Raman spectrometer system possessed a Spectra-Physics Ar<sup>+</sup> laser (model 2020-05) tuned to the exciting line at 514.5 nm. The radiation intensity at the samples was varied from 10 to 70 mW. The scattered radiation was passed through a Spex Triplemate spectrometer (Model 1877) coupled to a Princeton Applied Research OMA III optical multichannel analyzer (Model 1463) with an intensified photo diode array cooled to 233 K. Slit widths ranged from 60 to 550  $\mu\text{m}$ . The overall resolution was better than  $2 \text{ cm}^{-1}$ . For the *in situ* Raman spectra of dehydrated samples, a pressed wafer was placed into a stationary sample holder that was installed in an *in situ* cell. Spectra were recorded in flowing oxygen at room temperature after the samples were dehydrated in flowing oxygen at 573 K.

### 2.3. Ethane oxidation

The catalysts (20 mg) were tested for the partial oxidation of ethane with oxygen at atmospheric pressure in the temperature range 760-880 K. The reactor consisted of a quartz tube of 6 mm o.d. (4 mm i.d.), where no void volume was permitted to avoid homogenous reaction from the gas phase. The  $O_2/C_2H_6$  molar ratio was 2 and  $He/O_2$  molar ratio was 4. The gas feed was controlled by means of mass flow controllers (Brooks). The total flow range was 15-60 mL/min. The reactor effluent was analyzed by an on-line Hewlett-Packard Gas Chromatograph 5890 Series-II fitted with a thermal conductivity detector. Chromosorb 107 and Molecular Sieve 5A packed columns were used with a column isolation analysis system. The TOF (turnover frequencies, number of ethane molecules converted per surface vanadia species per second) were calculated assuming that all the supported vanadium oxide is active, in agreement with the absence of tridimensional aggregates of vanadium oxide (100 % dispersion).

## 3. RESULTS

### 3.1. Characterization.

The oxide supports used have the surface areas reported in Table 1 and a wide range of vanadium oxide loading on the supports has been prepared. The values presented in Table 1 correspond to monolayer coverage of vanadium oxide. The monolayer coverage can not be determined by theoretical calculation based on the coverage per  $VO_x$  unit (2), since the dispersion requires an interaction with the support and the monolayer coverage does not only rely on the surface area of the support, but also on its chemical nature. The monolayer coverage of surface vanadium oxide has been determined by Raman spectroscopy and XPS. The low monolayer coverage for the silica support is due to the low surface density of hydroxyl groups. The highly dispersed surface vanadium oxide species are characterized by a Raman band at ca.  $1030\text{ cm}^{-1}$  (Table 1), characteristic of a highly dispersed surface vanadium oxide species. At higher vanadia loadings, crystalline  $V_2O_5$  species dominate (strong Raman band at  $994\text{ cm}^{-1}$ ), and present a significantly different spectrum. The supported vanadium oxide sample with the highest vanadium oxide loading before the onset of crystalline vanadia corresponds to the monolayer catalyst. A parallel characterization has also been performed by XPS since the V/Support atomic ratio determined by XPS is very

Table 1  
Characterization of the supports and of the monolayer catalysts

Support	Surface Area BET ( $m^2/g$ )	Catalyst	% $V_2O_5$ (wt %)	Surface Area BET ( $m^2/g$ )	Vatoms per $nm^2$	V=O band ( $cm^{-1}$ )
$SiO_2$	337	12VSi	11,0	247	2,1	1039
$SiO_2-H_2O$	332	12VSi- $H_2O$	11,7	254	2,3	1039
$Al_2O_3$	222	25VAl	29,9	169	13,4	1026
$CeO_2$	36	4VCe	4,8	23	7,6	1028
$TiO_2$	45	6VTi	6,7	47	9,4	1030
$ZrO_2$	34	4VZr	3,0	31	8,2	1030
$Nb_2O_5$	57	5VNb	6,1	35	6,1	1031
5TiSi	280	10V5TiSi	ca. 10	--	--	1036

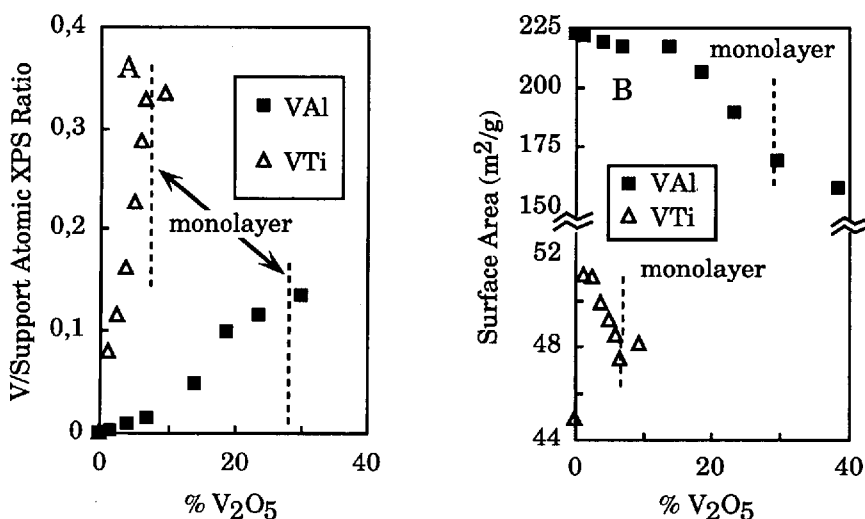


Figure 1. XPS V/Support atomic ratio (A) and Surface area (BET) vs. vanadium oxide loading of the representative series VTi and VAL.

sensitive to the dispersion degree of the surface vanadium species. Figure 1 presents the XPS V/Support atomic ratio determined for dehydrated samples on two representative series ( $V_2O_5/TiO_2$  and  $V_2O_5/Al_2O_3$ ). The V/Support atomic ratio increases linearly with the vanadium oxide loading and then levels off. This plateau corresponds to the formation of tridimensional aggregates of vanadium oxide, which Raman spectroscopy identifies as crystalline  $V_2O_5$ . The addition of vanadium oxide to the support continuously decreases the surface area. Close to the monolayer coverage, the surface vanadium oxide species show some polymerization (3,4) as evidenced by the Raman features observed at 920, 800, 600, and 550  $cm^{-1}$  (8).

### 3.2. Ethane oxidation

The oxidation of ethane over the supported vanadium oxide catalysts yields ethylene, CO, CO<sub>2</sub>, and minor amounts of acetaldehyde and formaldehyde. Methane production was not observed. The initial ethane conversions and TOF's for the catalysts with monolayer coverage of surface vanadium oxide are presented in Figure 2. There are significant differences in the activity of the different monolayer catalysts, where vanadium loading corresponds to the monolayer coverage. The treatment with water appears to increase the ethane conversion on silica-supported vanadium oxide monolayer catalysts. The TiO<sub>2</sub> and ZrO<sub>2</sub> supports result in the highest TOF. The catalysts with high activity deactivate also after few hours on stream, and the non-selective oxidation products are dominant. The selectivity-conversion plots are presented in Figure 3. Formaldehyde is observed at low conversion for all the catalysts but acetaldehyde can only be observed at low conversions on silica-supported catalysts.

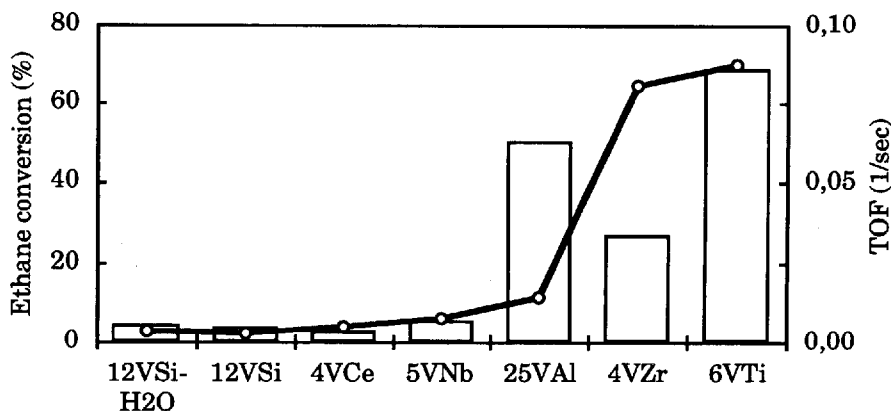


Figure 2. Conversion of ethane, absolute (columns) and T.O.F. numbers (circles) of the catalyst. Total flow 30 mL/min. Reaction temperature 823 K. W = 20 mg.  $O_2/C_2H_6 = 2$  molar and  $He/O_2 = 4$  molar.

The most active catalysts (6VTi, 4VZr, and 25VAl) show very high selectivity to deep oxidation, mainly CO, which increases at the expense of ethylene with ethane conversion. CO<sub>2</sub> is also present and its selectivity increases with conversion too. The catalyst 4VCe and 5VNb catalysts show an important trend to non-selective oxidation at low conversion levels. The selectivity to ethylene decreases markedly with conversion for 4VCe, and this trend is much smoother for 5VNb.

The TOF values for the alumina series evidences, that at the surface monolayer coverage of vanadium oxide, the vanadia sites behave differently: non-selective oxidation is dominant and the TOF of ethane and ethylene decreases (Figure 4). The continuous increase in oxygen TOF corresponds to the lower selectivity at vanadium oxide monolayer coverage on alumina. The titanium oxide supported vanadia, on the contrary, shows a more selective activity than alumina. The TOF's of ethylene are higher at submonolayer coverage (1VTi and 3VTi) and decrease at vanadia monolayer coverage. The TOF profiles show increase of CO and CO<sub>2</sub> with vanadia coverage but a significant decrease is observed for ethylene. These trends suggest a change in the environment of the vanadia sites as the surface coverage increases.

The high activity of titania-supported vanadium oxide and the selectivity of silica-supported vanadia suggests that a ternary catalyst (V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>) may possess positive characteristics. Vanadium oxide tends to preferentially coordinate to titania sites for the titania-silica supports (9). For this reason, the titania-silica support has been prepared with a highly dispersed titanium oxide surface species, strongly interacting with silica support, as determined by Raman spectroscopy and XPS (10). The activity of vanadium oxide on a highly dispersed titanium oxide surface species on silica is compared with the monolayers of

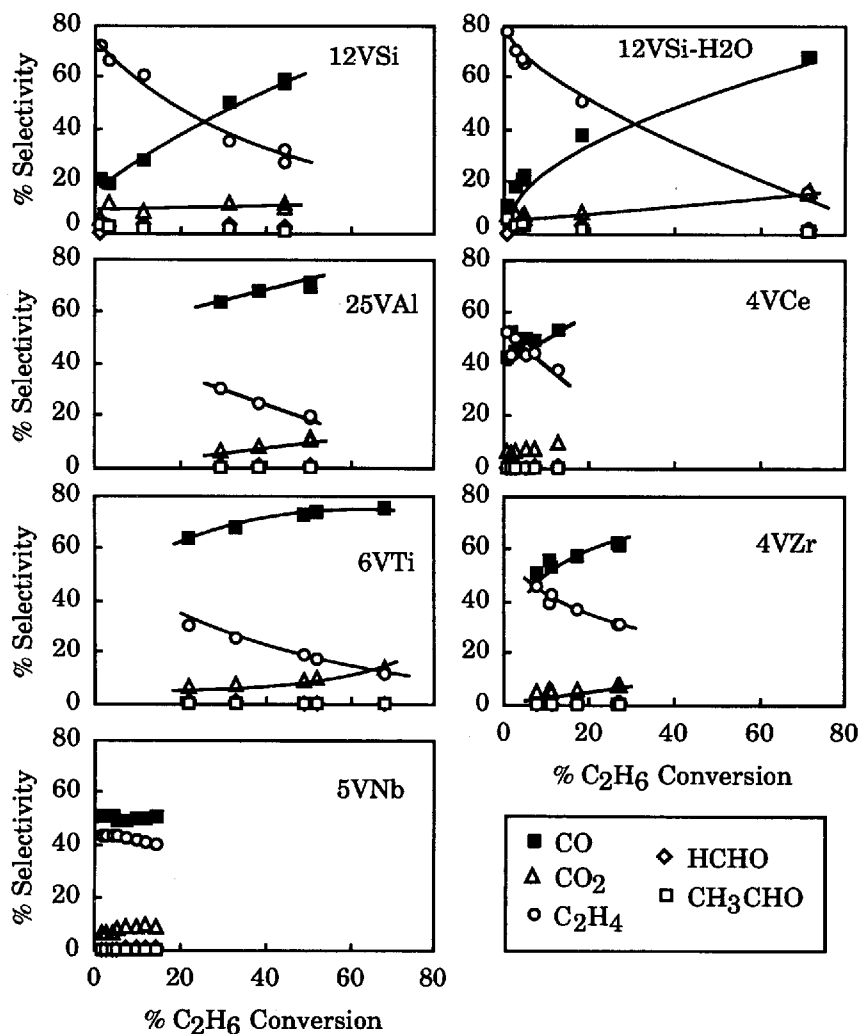


Figure 3. Selectivity conversion plots for the monolayers of vanadium oxide on the different supports. Reaction conditions: Total flow 30 mL/min. Reaction temperature 740-883 K.  $W = 20$  mg.  $O_2/C_2H_6 = 2$  molar and  $He/O_2 = 4$  molar.

vanadium oxide on silica and on titania in Table 2. As previously mentioned, the 6VTi catalyst is the most active system (highest TOF), the temperature to reach 15 % conversion of ethane is very low (750 K), but CO is the major oxidation product. The activities of the 12VSi and 10V5TiSi catalysts are similar but the selectivity to ethylene is higher for 10V5TiSi, and CO<sub>2</sub> is not produced for this catalyst.

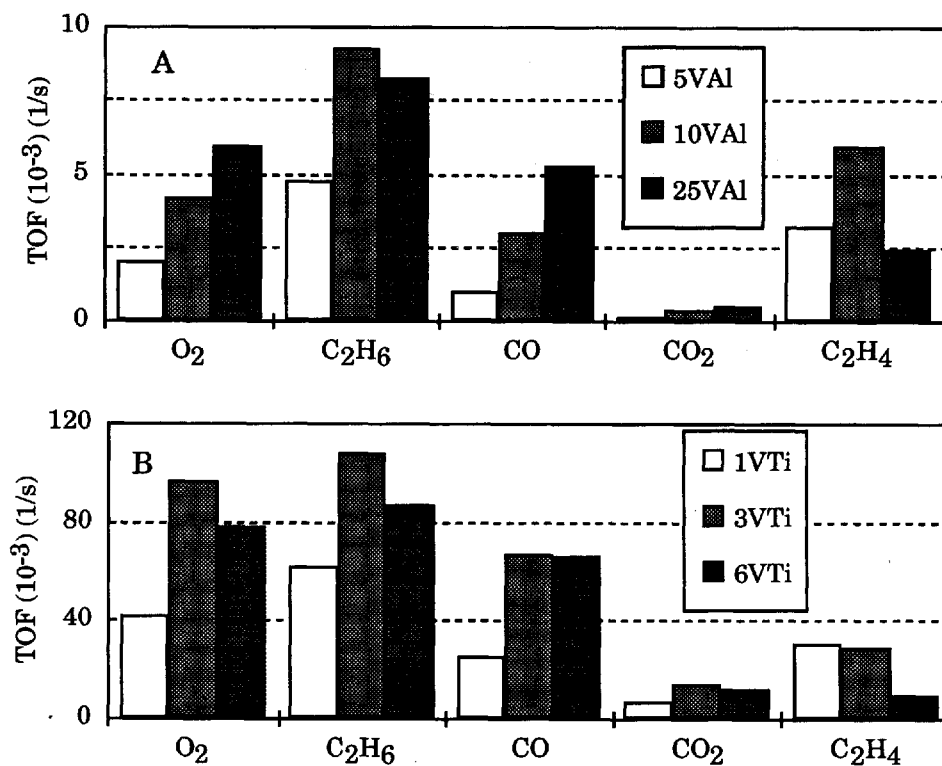


Figure 4. TOF numbers for the oxidation of ethane. Reaction conditions as in Figure 2.

Table 2

Selectivity of vanadium monolayer on silica and titania and titania-silica

Catalyst	Temp. (K)	Conversion (mole %)	% Selectivity				
			CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	HCHO	CH <sub>3</sub> CHO
25VAI	730	15.0	53.2	2.2	44.1	0.2	0.0
4VZr	794	15.0	55.4	5.4	39.1	0.1	0.0
4VCe	891	15.0	54.6	10.0	35.3	0.2	0.0
5VNb	908	15.0	51.1	8.9	39.7	0.3	0.0
12VSi-H <sub>2</sub> O	838	15.0	32.8	7.6	54.6	2.9	2.1
12VSi	847	15.0	31.7	8.3	55.9	2.9	1.1
6VTi	750	15.0	60.5	5.6	33.8	0.1	0.0
10V5TiSi	843	15.0	41.3	0.0	58.2	0.4	0.0

Reaction conditions as in Figure 2.

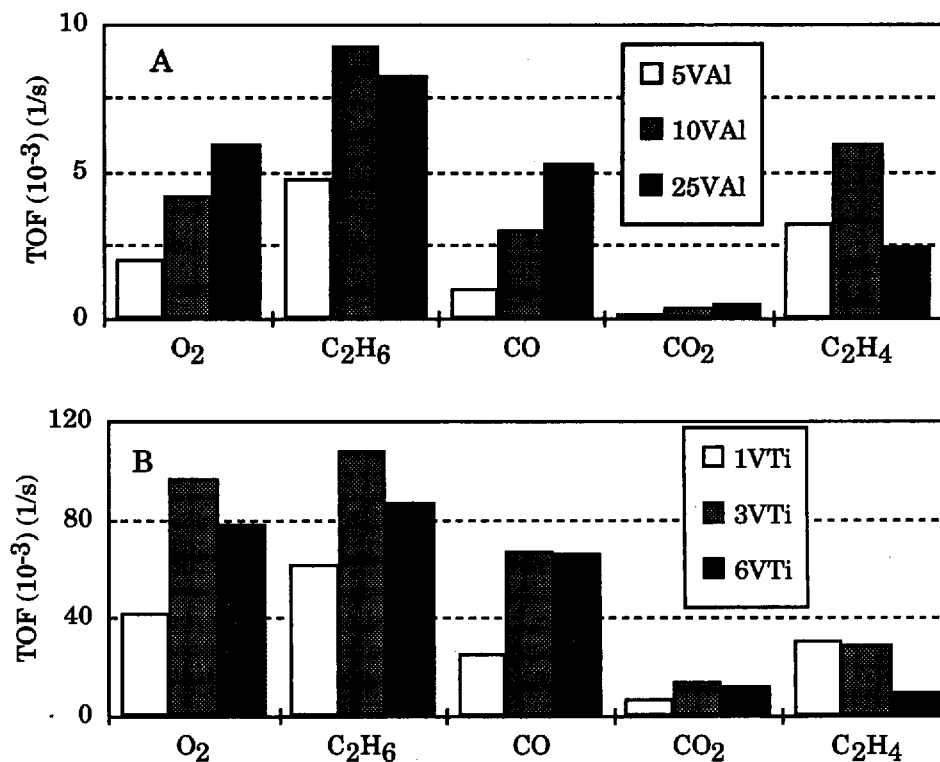


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Reaction conditions as in Figure 2.



#### 4. DISCUSSION

The dehydrated surface vanadium oxide species on the different supports possess the same structure as previous studies have already shown by Raman and  $^{51}\text{V}$ -NMR studies (3,11-13). Surface vanadium oxide species are present as isolated VO units containing one terminal V=O bond and three bridging V-O-Support bonds. Polymeric surface vanadium oxides are also present and their concentration increases with surface vanadia coverage. These species have one terminal V=O bond and possess bridging V-O-V and V-O-Support bonds. The linear increase of the XPS V/Ti atomic ratio is consistent with the dispersed nature of the surface vanadium oxide species at low coverage. The alumina supported series, exhibits a lower V/Al atomic XPS ratio at low vanadium oxide loadings, due to the higher surface area and porosity of the alumina support. The V/Al atomic XPS ratio is also linear with vanadia loading and supports the highly dispersed nature of surface vanadium oxide species on alumina at coverages below the monolayer. Water treatments of the silica support did not show appreciable differences between the two silica supported vanadium oxide catalysts since both catalysts perform very similar during the oxidation of ethane. Only higher activity is observed for the 12VSi-H<sub>2</sub>O.

The selectivity conversion trends suggests that ethane is initially oxidized to ethylene and that ethylene is further oxidized to CO. CO<sub>2</sub> could be a primary product, since its selectivity at zero conversion limit does not appear to be zero. The most important differences observed in catalytic behavior results from an interaction of the support with the active phase. For the same reaction conditions, the TOF's differ by more than an order of magnitude for the different catalysts. The changes in TOF's do not correspond with the changes in the terminal V=O Raman bands. A similar result has also been observed for the oxidation of methanol (14) and butane (8). Consequently, the active oxygen must be the bridging oxygen. At monolayer coverage, both V-O-V and V-O-Support bonds are present. Both may play a role in the reaction. The more reducible oxide titania and zirconia yield the most active catalysts (higher TOF's). Ceria is also a reducible oxide, which makes the supported vanadium oxide species more reducible than on alumina or silica, like titania and ceria (1,15), but TOF's on 4VCe are very low. Acidic supports, alumina and niobia, show some moderate activity and the non-acidic, non-reducible silica yields the lowest TOF's. Consequently, the activity of supported vanadium oxide for the oxidation of ethane follows the trends  $\text{TiO}_2 \sim \text{ZrO}_2 > \text{Al}_2\text{O}_3 > \text{Nb}_2\text{O}_5 > \text{SiO}_2$ . The low activity of 4VCe and 5VNb catalysts, despite their reducibility (4VCe) and acidity (5VNb) may be due to structural transformations by reaction of vanadia with the underlying oxide at the high temperatures required for ethane oxidation. Concerning selectivity, the more reducible oxide support systems show a high selectivity to deep oxidation (CO). 4VCe shows high selectivity to CO at low ethane conversion. The acidic supports, alumina and niobia, also yield CO as the main oxidation products. Only silica-supported vanadium oxide shows higher selectivities for ethylene. Acetaldehyde and formaldehyde are also produced on 12VSi and 12VSi-H<sub>2</sub>O.

The relevance of V-O-V bonds can be evaluated for the performance of  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  and  $\text{V}_2\text{O}_5/\text{TiO}_2$  at different surface coverages. Alumina supported vanadium oxide shows increasing TOF numbers for oxygen, CO and CO<sub>2</sub> as

vanadium oxide loading increases up to monolayer coverage. At monolayer coverage, where the (V-O-V) / (V-O-Support) ratio is expected to be highest, the TOF's of ethane and ethylene decrease, but TOF of oxygen, CO and CO<sub>2</sub> increase. This could be indicative of the higher reducibility of surface polymeric vanadium oxide species with respect to isolated surface vanadium oxide species (4,8), which appears to lead to a less active and selective catalyst. A similar trend is observed for VTi series: at monolayer coverage, ethane and ethylene TOF numbers decrease. For the titania-supported vanadium oxide catalysts, the TOF's for oxygen, CO and CO<sub>2</sub> do not increase at vanadia monolayer coverage as in the case of the VAl series. On the contrary, they decrease slightly, but isolated surface vanadium oxide species on titania are more reducible than isolated surface vanadium oxide species on alumina. This may account for the higher TOF(oxygen)/TOF(ethane) ratio observed on the VTi series. This ratio becomes closer for VTi and VAl series at monolayer coverage, where both series are expected to show a higher reducibility of the surface vanadium oxide species.

The ternary V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> catalyst shows interesting structural and catalytic properties. Surface vanadium oxide species preferentially coordinate to titania sites in the TiO<sub>2</sub>/SiO<sub>2</sub> supports (8). However, the use of a titania-silica support prepared so that titanium oxide is highly dispersed and strongly interacting with silica support results in titania with different characteristics to pure titania. The titania-silica support used here has 20% of the titanium atoms in tetrahedral coordination as determined by XPS and no crystalline aggregates of titania are formed, as determined by Raman spectroscopy (10). The V=O mode observed for the dehydrated 10V5TiSi catalyst is at 1036 cm<sup>-1</sup>, much closer to that of silica-supported vanadium oxide than to that of titanium-supported vanadium oxide (Table 1). The surface vanadium oxide species are isolated (100 % dispersion) and must also have a different coordination environment (probably anchored on both, titania and silica sites) that yields an activity similar to that on 12VSi but more selective, since no CO<sub>2</sub> is formed and the selectivity of ethylene increases. The lower selectivity of oxygen-containing products suggest that vanadia species on the highly dispersed titania-on-silica supports may be less reducible than on the pure constituting oxide supports.

## 5. CONCLUSIONS

The surface vanadium oxide species on silica, water-treated silica, alumina, ceria, titania, zirconia, niobia and titania-silica have been characterized and studied for the selective oxidation of ethane.

The terminal V=O bond does not appear to be directly involved in the reaction (no correlation with TOF). However, the bridging V-O-V or V-O-Support bonds appear to be critical for the oxidation of ethane. The nature of the V-O-Support bond is determined by the specific support. Bonding to a reducible support metal ion yields active catalysts (e.g. 6VTi and 4VZr). Acidic supports show some activity, but much lower than the reducible ones. The silica support is not reducible and does not possess acidic sites and shows the lowest TOF numbers. However, silica-supported vanadium oxide catalysts possess the highest selectivity. The very low activity of 4VCe and 5VNb could originate from a reaction of vanadia with the underlying support. The surface coverage increases

the (V-O-V) / (V-O-Support) ratio. Polymeric surface vanadium oxide species are more reducible than isolated surface vanadium oxide species in the presence of butane (15). If we assume a similar trend of reducibility with ethane than with butane, it turns out that more reducible surface vanadium oxide species are less active and selective. This effect is more evident for the VAl series than for the VTi series, since the isolated surface vanadium oxide species on alumina are much less reducible than on titania. All the catalysts that show higher reducibility, either due to its interaction with the support or due to its surface polymerisation show lower selectivity. The surface vanadium oxide species have a different environment for 10V5TiSi catalyst, which yields an activity similar to that of 12VSi but is more selective. Further research is going on to fully understand the environments of vanadia sites in this catalyst.

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