



# Oxidative dehydrogenation of ethanol to acetaldehyde on $V_2O_5/TiO_2-SiO_2$ catalysts obtained by grafting vanadium and titanium alkoxides on silica

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

## Abstract

Oxidative dehydrogenation of ethanol to acetaldehyde has been performed on vanadium based catalysts prepared by grafting on titania–silica supports with different procedures. A comparison of the performances of the prepared catalysts in terms of activity and selectivity has been made. Grafting technique gives place to well dispersed catalysts that resulted more selective than catalysts prepared by impregnation. In particular, very selective catalysts have been obtained by grafting vanadium–titanium bimetallic alkoxides directly on silica support. The effect of both the preparation methods and the used supports on the catalytic performances have been studied and an attempt to correlate the observed properties with the obtained results has been made.

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## 1. Introduction

Catalysts of  $V_2O_5$  supported on  $TiO_2$  or  $SiO_2$  have been studied by different authors in the selective oxidation of alcohols to aldehydes [1,2]. In particular, it has been observed that both pure  $V_2O_5$  [3] and  $V_2O_5$  supported on  $SiO_2$  [4] are active and selective in the oxidative dehydrogenation of ethanol to acetaldehyde. The properties of vanadium oxide, supported on different carriers, such as: silica, alumina, titania, have been investigated [1,2,5] and it is possible to conclude that the nature of vanadium oxide dispersed

phase strongly depends on the interaction between vanadium oxide and the support. It is well known, for example, that  $TiO_2$  in the form of anatase interacts very strongly with vanadium oxide favouring molecular dispersion of the active phase [6,7]. However,  $V_2O_5$  directly supported on  $TiO_2$  presents some drawbacks that are: limited specific surface area and lower resistance to sintering than other oxides. It is then known that silica, on the contrary, produces a weak interaction with vanadium oxide, therefore,  $V_2O_5$  supported on silica, shows high tendency to agglomerates, during calcination, with the formation of a low dispersed active phase. A  $TiO_2$  support with high and thermostable specific surface area can be obtained by coating silica surface with  $TiO_2$  [8,9]. Different  $V_2O_5$  catalysts, supported on  $TiO_2-SiO_2$  mixed oxides have

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been prepared, for example, for the selective catalytic reduction of NO with NH<sub>3</sub> [10–15]. Quaranta et al. [16] have compared the properties of different catalysts, respectively, prepared by impregnating vanadium acetyl-acetonate, dissolved in ethanol solution, on TiO<sub>2</sub>-SiO<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> supports, and their performances in the oxidative dehydrogenation of ethanol to acetaldehyde [16]. The same authors have prepared the support TiO<sub>2</sub>-SiO<sub>2</sub> by coating silica with titania by treating silica with an excess of TiCl<sub>3</sub>. The obtained support has been used to prepare the corresponding V<sub>2</sub>O<sub>5</sub> impregnated catalyst. Catalyst of the type V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> have shown about the same activity of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, but higher selectivity to acetaldehyde. The same authors have also studied the effect of titanium amount in the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> systems on the oxidative dehydrogenation (ODH) of ethanol [17].

In the present work a TiO<sub>2</sub>-SiO<sub>2</sub> supports have been prepared by a multistep grafting of titanium tetra-isopropoxide on silica following a procedure described in more detail elsewhere [9,18,19]. This support, together with a simple SiO<sub>2</sub> support, have been employed in the preparation of V<sub>2</sub>O<sub>5</sub> based catalysts by grafting vanadyl tri-isopropoxide with three different grafting procedures: (a) grafting vanadyl tri-isopropoxide, dissolved in *n*-hexane, on a TiO<sub>2</sub>-SiO<sub>2</sub> support; (b) grafting vanadyl tri-isopropoxide, dissolved in isopropanol and partially hydrolysed, by a controlled procedure, before grafting on a TiO<sub>2</sub>-SiO<sub>2</sub> support; (c) grafting, directly on uncoated SiO<sub>2</sub> support, mixtures of titanium and vanadyl alkoxides, dissolved in isopropanol and submitted to partial hydrolysis, before grafting. Partial hydrolysis of vanadyl tri-isopropoxide, before grafting on TiO<sub>2</sub>-SiO<sub>2</sub> support, has been made with the aim to evaluate the effect of vanadium aggregation on the catalytic performances. On the contrary, the scope of the partial hydrolysis of mixtures of titanium and vanadyl alkoxides was to obtain vanadium–titanium bimetallic alkoxides in isopropanol solution that can be anchored directly on a SiO<sub>2</sub> support with an opportune molar ratio between the two metals. In this way, the vanadium based catalyst preparation, having a favourable TiO<sub>2</sub> chemical environment, is largely simplified. In the meantime, obtained catalysts resulted more dispersed and more selective in the mentioned reaction. For a useful comparison, some catalysts have also been prepared in a tradi-

tional way by impregnation. In this work, the effects of the preparation methods and of the used supports, on the properties and catalytic performances, have been studied and an attempt has been made to correlate the observed properties with the obtained performances.

## 2. Experimental

### 2.1. Catalysts and supports preparation methods

The TiO<sub>2</sub>-SiO<sub>2</sub> support was prepared with a three steps grafting procedure using titanium isopropoxide, dissolved in toluene, and a commercial SiO<sub>2</sub>. We have used two different types of commercial silica: (i) a silica Aldrich (450 m<sup>2</sup> g<sup>-1</sup>), calcined at 500 °C for 2 h; (ii) a silica Grace S432 (305 m<sup>2</sup> g<sup>-1</sup>), calcined at 500 °C for 2 h, in one case, and for 8 h in another one. The amount of titanium isopropoxide, dissolved in toluene and used in each grafting step, roughly corresponds to a monolayer or to a moderate excess with respect to a monolayer, by assuming a conventional stoichiometry of 1 hydroxyl for 1 alkoxide molecule. Silica, after calcination, at 500 °C, for 2–8 h, was contacted with the mentioned solution by refluxing, at the boiling point of the solvent, for 6 h. Then, the solid has been recovered by filtration, washed with toluene, dried at 100 °C, steamed for 2 h at 130–190 °C for eliminating, by hydrolysis, the residual alkoxide groups from the surface and finally calcined at 500 °C. The described procedure has been repeated three times to obtain TiO<sub>2</sub>-SiO<sub>2</sub> support, that is, silica well coated with an amount of TiO<sub>2</sub> greater than the one correspondent to a monolayer. Some properties of the obtained silica coated supports are reported in Table 1. In the same Table are also summarised the differences in both the adopted preparation procedures such as: the type of silica and the amounts of titanium alkoxide used for each grafting step. The amount of grafted titanium was determined after dissolution in concentrated sulphuric acid, by reacting with H<sub>2</sub>O<sub>2</sub>, as reported by Snell and Etre [20]. More details concerning preparation methods, supports properties and amounts of reagents employed are reported in Table 2 and in previous papers [9,18,19]. The density of the OH groups on the silica surface was determined by means of thermogravimetric analysis (TGA) or by

Table 1  
Some properties of the used supports and catalysts

Supports and catalysts	Acronym	Preparation method	Grafting solvent	Ti(OR) <sub>4</sub> used for each step (mmol g <sup>-1</sup> )	TiO <sub>2</sub> supported (mmol g <sup>-1</sup> )	BET area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>2</sub> O <sub>5</sub> supported (wt.%)	O <sub>reducib</sub> /V <sub>supported</sub>
SiO <sub>2</sub> (Aldrich)	SA	–	–	–	–	450	0.72	–	–
SiO <sub>2</sub> (Grace)	S	–	–	–	–	305	1.02	–	–
TiO <sub>2</sub>	T	–	–	–	–	125	–	–	–
TiO <sub>2</sub> -SiO <sub>2</sub> (Aldrich)	TSMA	Grafting	Toluene	2.27	3.3	355	0.51	–	–
TiO <sub>2</sub> -SiO <sub>2</sub> (Grace)	TSM1	Grafting	Toluene	1.37	2.2	225	0.76	–	–
TiO <sub>2</sub> -SiO <sub>2</sub> (Grace)	TSM	Grafting	Toluene	0.95	1.4	299	0.27	–	–
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	V <sub>i</sub> /T	Impregnation	–	–	–	62	–	6.0	<0.01
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	VH/T	Grafting	<i>n</i> -Hexane	–	–	70	–	5.3	0.2
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	V <sub>i</sub> /TSMA	Impregnation	–	–	–	240	–	6.0	0.3
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	VH/TSMA	Grafting	<i>n</i> -Hexane	–	–	200	–	6.0	0.3
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	VH/TSM1	Grafting	<i>n</i> -Hexane	–	–	–	0.36	2.0	0.3
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	VH/TSM	Grafting	<i>n</i> -Hexane	–	–	249	0.29	0.8	0.7
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	V <sub>h</sub> I/TSM	Grafting	2-Propanol	–	–	314	0.26	0.9	0.6
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	VI/TSM	Grafting	2-Propanol	–	–	214	0.24	0.5	1.0
V <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> /SiO <sub>2</sub> <sup>a</sup>	(T <sub>h</sub> -V)I/S	Grafting	2-Propanol	–	–	–	–	0.9	–
V <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> /SiO <sub>2</sub> <sup>b</sup>	(V-T) <sub>h</sub> I/S	Grafting	2-Propanol	–	–	–	–	0.8	–

<sup>a</sup> H<sub>2</sub>O/Ti = 1.

<sup>b</sup> H<sub>2</sub>O/(V-T)<sub>h</sub> = 1; for both catalysts Ti/V = 12.

electrochemical titrations, as previously reported [9]. Silica supports, coated of titania with the three steps grafting procedure were then contacted with different solutions of vanadyl tri-isopropoxide, dissolved in *n*-hexane or isopropanol, at room temperature, for 24 h, under He atmosphere. After reaction the samples were filtered, washed with the used solvent, dried

at 105 °C, steamed at 190 °C for 2 h and calcined, at 500 °C, for 2 h. Vanadium load was determined by atomic adsorption spectroscopy, after dissolution in concentrated sulphuric acid. In Table 1 a list of all the prepared catalysts is reported, together with the conditions adopted for the preparation, the loading of TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> and other properties. In the last column

Table 2  
Reagents employed in the preparation of supports and catalysts

Supports and catalysts	Acronym	Preparation procedure	Amount of solid (g)	Volume of solvent (ml)	Ti(OR) <sub>4</sub> (g)	VO(OR) <sub>3</sub> (g)	Water (g)	NH <sub>4</sub> VO <sub>3</sub> (g)
TiO <sub>2</sub> -SiO <sub>2</sub> (Aldrich)	TSMA	A	6	60	3.866	–	–	–
TiO <sub>2</sub> -SiO <sub>2</sub> (Grace)	TSM1	A	6	60	2.334	–	–	–
TiO <sub>2</sub> -SiO <sub>2</sub> (Grace)	TSM	A	6	60	1.619	–	–	–
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	V <sub>i</sub> /T	B	2.5	30	–	–	–	0.225
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	VH/T	C	6	75	–	0.853	–	–
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	V <sub>i</sub> /TSMA	B	2.5	30	–	–	–	0.225
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	VH/TSMA	C	6	75	–	0.967	–	–
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	VH/TSM1	C	6	75	–	0.322	–	–
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	VH/TSM	C	6	75	–	0.129	–	–
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	V <sub>h</sub> I/TSM	D	4	40	–	1.035	0.076	–
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	VI/TSM	C	4	40	–	0.537	–	–
V <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> /SiO <sub>2</sub>	(T <sub>h</sub> -V)I/S	E	3	40	1.125	0.081	0.071	–
V <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> /SiO <sub>2</sub>	(V-T) <sub>h</sub> I/S	F	3	40	1.125	0.081	0.077	–

of Table 1 is also reported an index of the vanadium dispersion, corresponding to oxygen uptake for vanadium atom, determined by TPR/TPO with oxygen pulses. The acronyms used for the catalysts are easily interpretable and summarise both the preparation methods and the compositions. We have named, for example: S, SiO<sub>2</sub>; T, TiO<sub>2</sub>; TSM and TSM1, Grace silica coated with TiO<sub>2</sub> by the three steps grafting procedure and by following two different calcinating procedures: TSMA, Aldrich silica coated with TiO<sub>2</sub> by the three steps grafting procedure; H, *n*-hexane solvent of the precursor; I, isopropanol solvent. Suffix h corresponds to a hydrolysed alkoxide. Catalysts of VH/TSM and VH/TSM1 series, for example, were prepared by grafting vanadyl tri-isopropoxide dissolved in *n*-hexane on TiO<sub>2</sub>-SiO<sub>2</sub> supports. Catalyst V<sub>h</sub>I/TSM was prepared by grafting partially hydrolysed vanadyl tri-isopropoxide, dissolved in 2-propanol, on the corresponding support. Hydrolysis was carried out, in this case, by dissolving 1 ml of vanadyl tri-isopropoxide in 4 ml of 2-propanol and by adding a stoichiometric amount of water (1 mol of water/1 mol of vanadyl tri-isopropoxide) containing traces of HCl acting as catalyst. The aim was initially to obtain a less dispersed catalysts by favouring through the hydrolysis the aggregation by condensation of the vanadyl tri-isopropoxide molecules but the presence of the parent alcohol largely prevent the condensation reaction. Moreover, the grafting yield in this case is not quantitative always for the influence of the solvent (the parent alcohol) on the grafting equilibrium. As a consequence, small amounts of vanadium oxide (about 1 wt.%) are loaded on the support. Catalysts of (V-T)I/S series have been prepared by grafting a bimetallic vanadium–titanium alkoxide, dissolved in isopropanol, directly on SiO<sub>2</sub>. The bimetallic alkoxide has been obtained in two different ways: by hydrolysing, for example, titanium tetra-isopropoxide with a stoichiometric amount of water and reacting it with vanadyl tri-isopropoxide (T<sub>h</sub>-V)I/S, or by hydrolysing a mixture of the two alkoxides both dissolved in isopropanol (T-V)<sub>h</sub>I/S. The molar ratio titanium–vanadium has been kept 12:1 in both cases. For these catalysts the hydrolysis step had the objective to obtain a bimetallic precursor, formed by condensation of the two alkoxide species, that can then be anchored directly on silica surface.

Some catalysts have been prepared, at last, in a traditional way by wet impregnation of the support with an ammonium vanadate aqueous solution [21]. The suffix i indicates catalysts prepared by impregnation.

To summarise we adopted six different catalysts preparation procedures indicated in Table 2 by (A)–(F). Details about these procedures are reported as follows.

- (A) The amount of titanium alkoxide reported in Table 2 was dissolved in the solvent and the obtained solution was contacted with the solid under solvent reflux for 6 h. The solid was then filtered, washed and dried. This procedure was repeated three times.
- (B) The amount of solid support reported in Table 2 was contacted with a solution of ammonium metavanadate and oxalic acid (0.25 g) and heated. When water was completely evaporated the solid was recovered and calcined at 500 °C for 18 h.
- (C) This is the standard grafting procedure. The amount of alkoxide indicated in Table 2 was used to prepare a solution with the reported solvent and this solution was put in contact with the related amount of solid. After the reaction, the solid was filtered, washed, dried, steamed with water vapour at 150 °C for 2 h and calcined at 500 °C for 2 h.
- (D) A partially hydrolysed vanadyl tri-isopropoxide was prepared by a preliminary hydrolysis step in which 1:1 molar ratio of water/alkoxyde was used in the presence of traces of HCl as catalysts. The obtained precursor is then contacted with the reported amount of solid and the preparation proceed as in item (C).
- (E) Bimetallic precursor have been prepared by previously hydrolysing titanium tetra-isopropoxide with the reported amount of water (molar ratio 1:1), containing traces of HCl, and reacting then with vanadyl tri-isopropoxide. The obtained solution was contacted with the reported amount of solid as for item (C).
- (F) Bimetallic precursor have been prepared with a procedure similar to that reported at point E but now the hydrolysis has been performed on a mixture of the two different alkoxides of vanadium and titanium dissolved in 2-propanol. A molar ratio of 1:12 for V:Ti was adopted for preparing

the mixture and water, containing traces of HCl, was added in order to obtain a molar ratio water/(V + Ti) equal to 1.

## 2.2. Catalysts and supports characterisation methods

The morphological characterisation and elemental composition of the catalyst were carried out by SEM on a JEOL JSM 5600LV instrument coupled with an EDX analyser. XRD patterns were recorded on a X3000 Seifert diffractometer equipped with a lithium fluoride monochromator on the diffracted beam. The scans were collected within the range of 4–44 ( $2\theta$ ) using Mo K $\alpha$  radiation. Diffuse reflectance spectra were obtained on a UV-Vis scanning spectrophotometer Shimadzu AV2101, equipped with an integrating sphere, using BaSO<sub>4</sub> as reference. UV-Vis spectra were recorded in the diffuse reflectance mode ( $R$ ) and transformed to a magnitude proportional to the extinction coefficient ( $K$ ) through the Kubelka–Munk function ( $F(R)$ ). FTIR and DRIFT spectra have been made by using a NICOLET AVATAR 360 instrument. Samples were examined in a DRIFT cell, at room temperature, after the outgassing in vacuum, at 400 °C, for 1 h. Textural analysis was carried out on a Thermoquest Sorptomatic 1990 Instrument (Fisons Instruments), by determining the nitrogen adsorption/desorption isotherms, at 77 K. Before analysis, the samples were heated overnight under vacuum up to 473 K (heating rate = 1 K min<sup>-1</sup>). The specific surface area and pore distributions were determined by using the BET and Dollimore–Heal methods [22,23].

### 2.2.1. Catalytic runs

All the catalysts were tested in the oxidative dehydrogenation of ethanol to acetaldehyde. The tests were carried out in a continuous flow fixed-bed microreactor, that is, a stainless steel tube of 10 mm inner diameter operating at atmospheric pressure. The explored temperature range was 100–200 °C, with a residence time of ethanol normally kept at  $W/F = 26.4 \text{ g}_{\text{cat}} \text{ h}^{-1} \text{ mol}$  of ethanol. The fed reacting mixtures ethanol–oxygen–helium was: ethanol (Fluka 99.9%) 1.1 ml h<sup>-1</sup> (as liquid), oxygen (SOL 99%) 7.7 ml h<sup>-1</sup> and helium (SOL 99%) 22 ml h<sup>-1</sup> as diluent and carrier gas for GC. Reagents and products were analysed by on-line gas chromatograph HP 5890A using a

column Restek Rt-Q plot 30 m × 0.32 mm. Conversion and selectivities to products were calculated on a carbon atom basis. The conversion corresponds to the ratio between reacted and fed ethanol, while, the selectivities are calculated as ethanol transformed to each product with respect to the total ethanol reacted.

## 3. Results and discussion

All the performed catalytic runs are reported in Table 3. From these data, reaction rates can be calculated at different temperatures and an estimation of the activation energy can be made. We have found a value falling in the range 16–20 kcal mol<sup>-1</sup> in agreement with Oyama and Somorjai [2]. As it can be seen from Table 3, acetaldehyde is always the main reaction product. Observed by-products, in order of importance are: acetic acid, acetals and carbon dioxide. Small amounts of ethyl acetate, ethyl ether and ethylene have sometime observed.

### 3.1. Comparison of the performances of catalysts, respectively, prepared by grafting and impregnation

From the data concerning catalytic tests, reported in Table 3, it is possible to observe, first of all, that catalysts prepared by grafting, with high vanadium load, are less active but more selective than the corresponding catalysts prepared by impregnation. This can be appreciated also in Figs. 1 and 2, where are reported, respectively, the conversion as a function of the temperature, and the selectivity to acetaldehyde, as a function of the ethanol conversion, for catalysts both impregnated and grafted on, respectively, TiO<sub>2</sub> and TiO<sub>2</sub>-SiO<sub>2</sub> supports, all containing about the same amount of V<sub>2</sub>O<sub>5</sub>, corresponding to 5–6 wt.%.

### 3.2. Effects of dispersion, vanadium load and solvent on the catalysts performances

In Fig. 3, the conversion obtained at different temperatures and the selectivities to acetaldehyde, as a function of the conversion, for different catalysts, all prepared by grafting, are reported. As it can be seen, by comparing the performances of the catalysts VH/T SMA and VH/T SM1, activities roughly increase with the vanadium load. However, also the dispersion

Table 3  
Results of catalytic test reaction

Catalyst	V <sub>2</sub> O <sub>5</sub> (wt.%)	Temperature (°C)	Ethanol conversion	Selectivities			
				Acetaldehyde	Acetic acid	Acetals	CO <sub>2</sub>
Vi/T	6	98	0.0592	1.0000	0	0	0
		120	0.1741	0.8350	0.0250	0.1400	0
		142	0.8067	0.5040	0.0470	0.1440	0.2780
		155	0.8464	0.4830	0.0530	0.1480	0.3050
		177	0.9187	0.4180	0.0870	0.1400	0.3280
VH/T	5.3	119	0.1250	0.9500	0.0310	0	0
		142.5	0.5630	0.7650	0.0310	0.0250	0.1800
		157	0.6970	0.7070	0.0110	0.0950	0.1870
Vi/TSMA	6	100	0.2033	0.8413	0.0279	0.1308	0
		120	0.4764	0.5656	0.0794	0.2123	0.1381
		154	0.8741	0.4797	0.0701	0.2069	0.2270
		174	0.9078	0.3809	0.1339	0.0933	0.3679
VH/TSMA	6	100	0.0748	1.0000	0	0	0
		120	0.1790	0.8727	0.0257	0.1015	0
		141	0.3386	0.8360	0.0420	0.1220	0
		157	0.7647	0.6760	0.0550	0.1420	0.1270
		176	0.8095	0.5820	0.0840	0.1350	0.1990
VH/TSM1	2	104	0.0108	1.0000	0	0	0
		121	0.0446	0.9650	0.0350	0	0
		142	0.0941	0.8190	0.0380	0.1430	0
		155	0.1557	0.8740	0.0470	0.0790	0
		177	0.4129	0.7580	0.0740	0.0700	0.0920
VH/TSM	0.8	104	0.0222	0.8737	0.0189	0.1074	0
		124	0.0767	0.9070	0.0200	0.0270	0
		142	0.2882	0.8670	0.0290	0.0730	0
V <sub>h</sub> I/TSM	0.9	104	0.0334	0.9280	0.0240	0	0
		124	0.0817	0.8770	0.0330	0.0400	0
		144	0.2307	0.8510	0.0420	0.0700	0
		161	0.5437	0.7860	0.0630	0.0940	0.0530
		184	0.7641	0.7000	0.0860	0.1050	0.0930
VI/TSM	0.5	95	0.0087	0.9520	0.0480	0	0
		112	0.0153	0.9540	0.0460	0	0
		131	0.0782	0.8720	0.0360	0.0340	0
		149	0.1425	0.8350	0.0530	0.0470	0
		166	0.2488	0.6970	0.0640	0.1010	0.1240
		181	0.5527	0.7310	0.0750	0.1030	0.0770
(T <sub>h</sub> -V)I/S	0.9	93	0.0029	1.0000	0	0	0
		112	0.0086	0.9280	0	0	0
		133	0.0361	0.9660	0.0340	0	0
		150	0.1577	0.9920	0.0080	0	0
		172	0.2126	0.9310	0.0110	0.0350	0
		190	0.5093	0.8910	0.0090	0.0470	0.0040
(V-T) <sub>h</sub> I/S	0.8	94	0.0025	1.0000	0	0	0
		113	0.0090	0.9600	0.0400	0	0
		131	0.0307	0.9800	0.0200	0	0
		158	0.1316	0.9230	0.0160	0.0280	0
		175	0.2777	0.9320	0.0170	0.0400	0

Catalyst weight 0.5 g; ethanol 1.1 ml h<sup>-1</sup>; oxygen 7.7 ml min<sup>-1</sup>; helium 22 ml min<sup>-1</sup>; W/F = 26.4 g<sub>cat</sub> (h mol ethanol)<sup>-1</sup>.

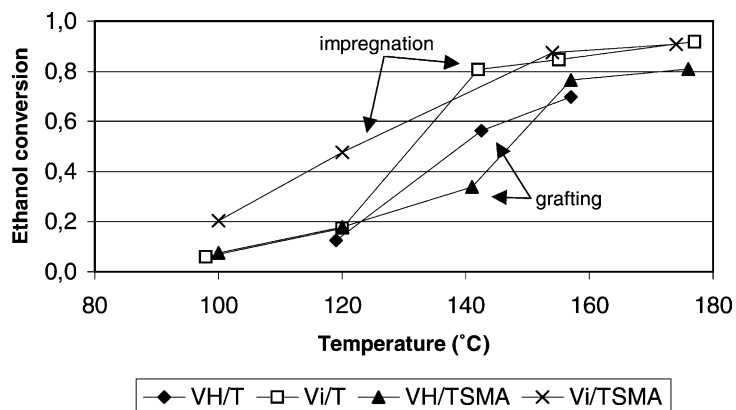


Fig. 1. A comparison of the activities of different catalysts obtained by grafting and impregnation.

(see last column of Table 1) seems to be an important factor in determining catalyst activity, because, catalysts that appear highly dispersed, such as VI/TSM, containing low vanadium charge, can be more active than catalysts containing more vanadium, such as VH/TSM1, but in a less dispersed form. Catalyst VI/TSM allows to point out also the influence of the solvent. The use of the parent alcohol, as a solvent, gives place to low grafting yields for the detrimental effect of the solvent on the grafting equilibrium reaction. However, catalyst prepared in this way have higher dispersion also for the effect of solvation, that is, vanadyl tri-isopropoxide results less aggregated in isopropanol than in *n*-hexane. By concluding, vanadium load and dispersion are key factors in determining catalytic activity. Despite the strong differences

observed in catalytic activities for the catalysts prepared by grafting, selectivities are poorly affected by both vanadium load and dispersion, being the selectivity trend with conversion quite similar for all these catalysts, as it can be appreciated in Fig. 3. A difference in selectivity is, on the contrary, observed by comparing grafted and impregnated catalysts, being selectivity of grafted catalysts significantly higher.

### 3.3. Influence of the preparation procedure on the catalytic performances

In Fig. 4, the conversions obtained, at different temperatures, and selectivities as a function of conversions, for catalysts containing comparable amounts of vanadia (about 1%), but prepared with different

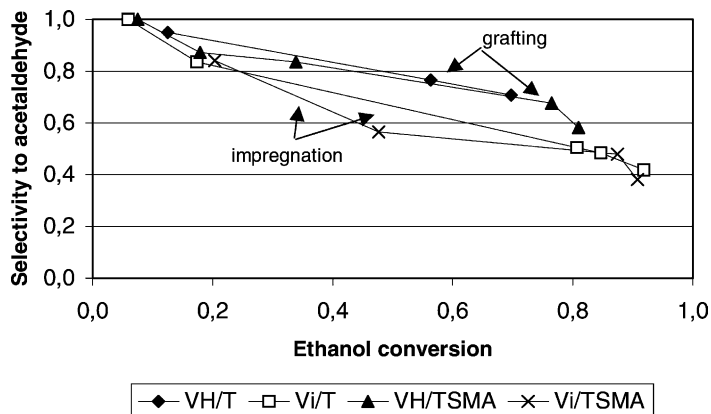


Fig. 2. A comparison of the selectivities shown by the different catalysts, respectively, prepared by grafting and impregnation.

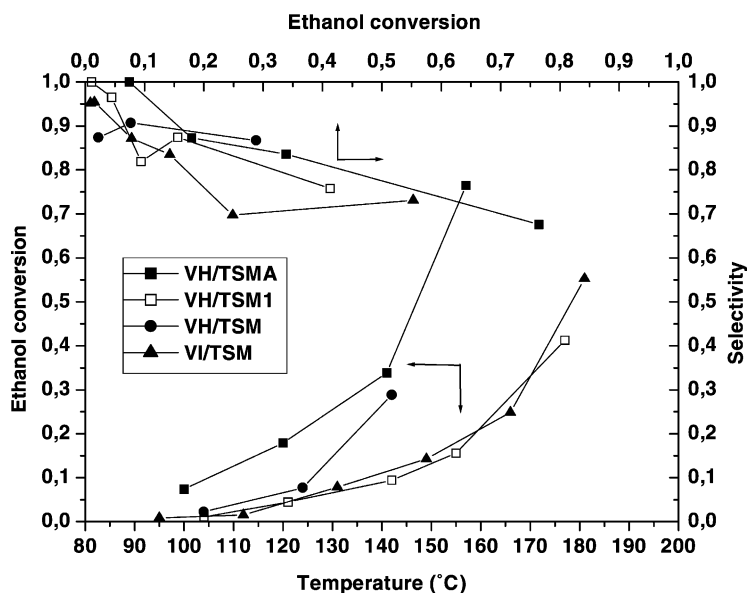


Fig. 3. A comparison of the activities and selectivities shown by the different catalysts prepared by grafting following different procedures.

procedures, are compared. As it can be observed, catalysts prepared by grafting, directly on silica, titanium–vanadium bimetallic alkoxide obtained by partial hydrolysis of titanium alkoxide, and then re-

acted with vanadium alkoxide (catalyst  $(T_h-V)I/S$ ) or by partial hydrolysis of a mixture of the two alkoxides (catalyst  $(T-V)_hI/S$ ), are less active but more selective than the other prepared catalysts. Selectivities

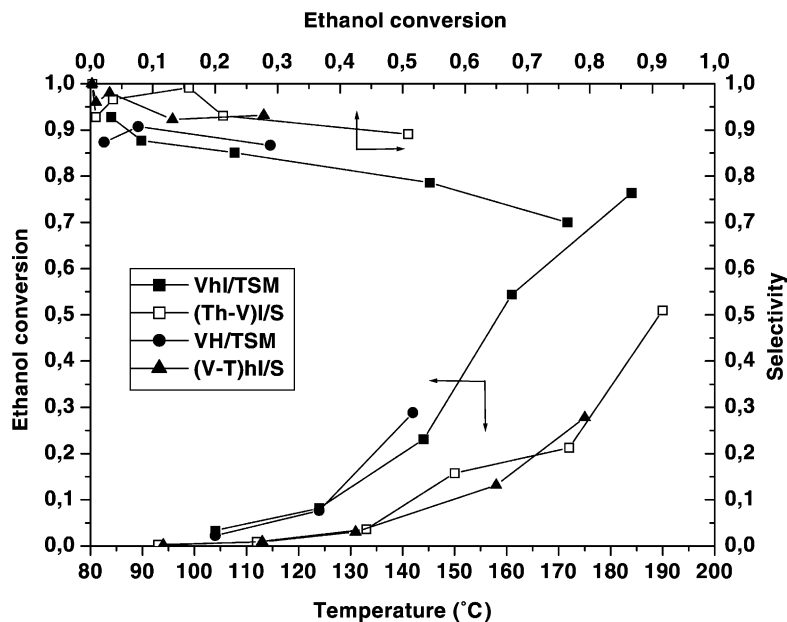


Fig. 4. A comparison of the activities and selectivities shown by the different catalysts prepared by grafting following different procedures.



shown by these catalysts are also more stable with the conversion than all the other tested catalysts. It is interesting to observe also that the catalyst, prepared by partially hydrolysing vanadyl tri-isopropoxide, dissolved in isopropanol before grafting on TiO<sub>2</sub>-SiO<sub>2</sub> support (V<sub>h</sub>I/TSM), has an activity that is comparable with the catalyst prepared by grafting vanadyl tri-isopropoxide, dissolved in *n*-hexane, on the same support. This, probably means that the two mentioned catalysts have similar dispersions, being the aggregation induced by the hydrolysis contrasted by the presence of the parent alcohol, that is, for this reason vanadium alkoxide aggregation by condensation was not achieved.

Surface area of TiO<sub>2</sub>-SiO<sub>2</sub> supports remains comparable with that of the original support also after three grafting steps. Pore volumes are, on the contrary, reduced for the appearance of micropores. In all cases, titania phase is largely amorphous with a small portion of crystalline phase in the form of anatase. Specific surface area of the prepared catalysts are reported in Table 1. Supporting vanadia, by both grafting and impregnation, normally gives place to a decrease of the specific surface area, also for a small vanadium charge. Pore distributions, on the contrary are poorly affected by the presence of vanadia on the support. The interpretation of these phenomena is quite difficult because many factors are involved in the different preparation steps. Consider, for example, grafting stoichiometry that can change according the adopted conditions, the steaming procedure and calcination that can give place to a deep surface modification.

### 3.4. Spectroscopic investigations

Spectroscopic investigations of all the mentioned catalysts have been made in other previous works, where, the same catalysts have been used in oxidative dehydrogenation of other molecule such as propane [24] and isobutane [25]. In those papers, the results of the spectroscopic investigations are reported in details, while, the main findings are here simply summarised with a look to the consequences for the specific examined reaction.

All the catalysts have shown a diffraction spectra quite similar to that of the support. However, we have never observed the presence of crystalline V<sub>2</sub>O<sub>5</sub>. The support is mainly constituted by an amorphous

part. Catalysts prepared by grafting vanadium from *n*-hexane solvent, on titania-silica supports, show the same morphological features observed on the corresponding supports. Grafted vanadium species are then supposed to be highly dispersed on the carriers. On the contrary, on catalysts of (V-T)I/S series, prepared by grafting bimetallic titanium-vanadium alkoxide directly on silica, has been noticed the presence of amorphous aggregates composed, according to EDX analysis, mainly of titanium and vanadium, while, vanadium is never present on the silica surface.

FTIR and DRIFT spectra have been collected for many supports and catalysts reported in Table 1. The absence of crystalline V<sub>2</sub>O<sub>5</sub> is confirmed, because, the corresponding band, at 1020 cm<sup>-1</sup>, is never observed, while absorption at 960–990 cm<sup>-1</sup> confirms the formation of polyvanadylic species, of low nuclearity, also at low vanadium charge [26]. The original SiO<sub>2</sub> support shows an intense band of absorption at 3747 cm<sup>-1</sup> corresponding to isolated silanol groups Si-OH [27,28]. This peak completely disappears as a consequence of the titanium alkoxide grafting. The spectrum for (T-V)<sub>h</sub>I/S and (T<sub>h</sub>-V)I/S shows many silanol groups, in agreement with the fact that, in this case, a bimetallic alkoxide of vanadium and titanium is directly grafted on silica, without forming a monolayer. Some useful information can be derived from the observation of the V-O-V absorption bands, in the range 550–800 cm<sup>-1</sup>, corresponding to an increase of the aggregation degree and a consequent decrease of the V<sub>2</sub>O<sub>5</sub> dispersion. Absorption bands of this type have been observed for all the catalysts of VH/TSM, VH/TSM1 and V<sub>h</sub>I/TSM type. For catalysts obtained from bimetallic precursors, subjected to hydrolysis (such as: (V-T)<sub>h</sub>I/S, (V<sub>h</sub>-T)I/S), polyvanadylic V-O-V absorption bands completely disappear. This means the presence of isolated monovanadylic species and conversely a prevalence of V-O-Ti bonds with respect to V-O-V ones.

### 3.5. Correlation between catalyst properties and catalytic behaviour

All the prepared catalysts have been tested in the ODH of ethanol, giving place to significant differences of both activities and selectivities. The group of catalysts prepared, for example, by grafting different amounts of vanadyl tri-isopropoxide, dissolved

in *n*-hexane, on a support of silica coated with an amount of TiO<sub>2</sub> greater than a monolayer, give place to almost quantitative grafting reaction (see catalysts of VH/TSM1 and VH/TSM type reported in Table 1). The activities of these catalysts resulted roughly related to the vanadium content, as it can be seen from Fig. 3. This behaviour suggests a good dispersion for all the catalysts prepared by grafting. This is not contradictory with the DRIFT analyses of these catalysts showing the presence of polyvanadylic groups, because, it is well known the tendency of V<sub>2</sub>O<sub>5</sub> to give monolayered structures on TiO<sub>2</sub> surfaces [29], until to reach a complete coverage. The apolar solvent *n*-hexane, favours the molecular aggregation giving place, at least, to a dimeric structure [30]. Activities to acetaldehyde of these catalysts are lower than the ones shown by impregnated catalysts, while selectivities are higher. This means that in general dispersion has a positive effect on selectivity giving place to uniform active sites that are more selective even less active. This is confirmed by the behaviour of the catalysts prepared by grafting vanadium–titanium bimetallic alkoxides, dissolved in isopropanol, directly on silica, and prepared by partial hydrolysis (catalysts (T<sub>h</sub>-V)I/S and (V-T)<sub>h</sub>I/S). Both catalysts have the same behaviour, probably because, the vanadium–titanium bimetallic alkoxide precursor formed is the same. Titanium alkoxide reacts more fastly than vanadium alkoxide giving place to mononuclear specie Ti(OR)<sub>3</sub>OH. This, can react with vanadyl tri-isopropoxide giving a bimetallic alkoxide.

It is interesting to point out that the most selective catalysts (T<sub>h</sub>-V)I/S and (V-T)<sub>h</sub>I/S do not show, at the DRIFT analysis, the presence of polyvanadylic groups in the wave number range 550–800 cm<sup>-1</sup>, while, these groups are present for both VH/TSM and V<sub>h</sub>I/TSM catalysts. This can be interpreted with the formation of isolated vanadium oxide groups directly bounded to titanium oxide grafted on the silica support. Therefore, the prevalence of V–O–Ti bonds in these catalysts with respect to V–O–V bonds in the others, could be the reason of the observed highest selectivity.

#### 4. Conclusions

We have confirmed that TiO<sub>2</sub> chemical environment has a positive effect in the ODH of ethanol to

acetaldehyde also for catalyst prepared by grafting. A new preparation method of vanadium based catalysts with a TiO<sub>2</sub> favourable environment has been realised in this work. The adopted preparation route related to catalysts (T<sub>h</sub>-V)I/S and (V-T)<sub>h</sub>I/S, is simpler and cheaper not requiring the long and expensive procedure of three steps grafting of titanium alkoxide on silica. Surprisingly, with this procedure we obtained also a remarkable improvement in the selectivity of the oxidative dehydrogenation of ethanol to acetaldehyde. An attempt has been made in order to explain the increase of the observed selectivities on the basis of catalysts properties and adopted preparation procedures.

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