



Oxidative dehydrogenation of propane using $V_2O_5/TiO_2/SiO_2$ catalysts prepared by grafting titanium and vanadium alkoxides on silica

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Abstract

The oxidative dehydrogenation (ODH) of propane have been studied on three different vanadium oxide catalysts, containing comparable amounts of vanadium. All the proven catalysts have been prepared by grafting but following different procedures. One has been prepared by grafting vanadyl tri-isopropoxide, dissolved in *n*-hexane on a support of silica coated with a multi-layer of TiO_2 . The support has been prepared by grafting in three different steps titanium alkoxide on silica. Another catalyst has been prepared by partially hydrolysing vanadyl tri-isopropoxide, dissolved in isopropanol, before grafting the obtained product on the same support. The third catalyst has been prepared by reacting partially hydrolysed vanadyl tri-isopropoxide with titanium alkoxide in isopropanol and anchoring then the reaction product, a vanadium–titanium bimetallic alkoxide, directly on silica. The first and second catalysts have similar activities and selectivities, while the third catalyst is less active but more selective than the other two ones. A kinetic approach has been made and a pseudo-first order kinetic law has been used to interpret the results. All the observed catalytic phenomena have been interpreted also with the aid of the several used characterisation techniques.

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1. Introduction

Propene is an important intermediate in the petrochemical industry largely requested to produce polypropylene, acrylic acid, acetone, etc. The increasing demand for propene in the industrial market and the interest in using a cheaper source such as propane has led to an increase in the research on the oxida-

tive dehydrogenation (ODH) of propane [1–11]. The ODH of propane could be much more convenient than the direct dehydrogenation requiring very high temperatures at which coking phenomena and catalyst deactivation normally occur. On the contrary, ODH is thermodynamically feasible at all temperatures, but requires selective catalysts in order to avoid the complete oxidation to CO and CO_2 . Recent works have shown that catalysts based on supported vanadium oxide are active and selective for the ODH of light alkanes [8,11–27]. Activities and selectivities of these catalysts depend, respectively, on the type of

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support adopted, the amount of charged vanadia, the degree of vanadia dispersion and the type of catalyst pre-treatments. The presence of TiO_2 on the surface favours the dispersion of V_2O_5 due to the strong interaction between titania and supported vanadium oxide. However, TiO_2 supports, normally, have low surface area and low mechanical and thermal resistance. On the contrary, SiO_2 weakly interacts with V_2O_5 favouring, therefore, a thermally induced agglomeration of V_2O_5 surface species. In a previous work [11], the grafting technique has been used to prepare vanadium catalysts supported on SiO_2 previously coated with a multi-layer of TiO_2 . Coatings of TiO_2 were obtained by grafting a titanium alkoxide on SiO_2 surface and repeating the grafting operation three times. Vanadyl tri-isopropoxide has then been grafted on the obtained $\text{TiO}_2/\text{SiO}_2$ support. Catalytic behaviours of $\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$ catalysts were tested in a previous work [11] on the ODH of propane for what concerns the effect of the amount of supported vanadium. On the basis of this work, it is interesting to observe, first of all, that by using the grafting technique for the preparation, it is possible to obtain catalysts with a relatively high amount of supported vanadium (more than 5 wt.%) without the formation of crystalline V_2O_5 . However, in the range investigated (2–10 wt.%), optimal activities and selectivities were obtained for catalysts containing about 5 wt.% of V_2O_5 . In the present work the grafting technique has been used again to prepare vanadium based catalysts. Three catalysts, prepared in different ways, containing comparable amounts of vanadium corresponding to about 1 wt.% of V_2O_5 , have been tested always in the ODH of propane. The first catalyst has been prepared by grafting vanadyl tri-isopropoxide dissolved in *n*-hexane on the already mentioned $\text{TiO}_2/\text{SiO}_2$ support, that is, SiO_2 coated with a multi-layer of TiO_2 . The second catalyst has been prepared by dissolving vanadyl tri-isopropoxide in 2-propanol and by hydrolysing partially the alkoxide with a stoichiometric amount of water before the grafting on the same support. The third catalyst has been prepared by reacting partially hydrolysed vanadium alkoxide with titanium alkoxide ($\text{V}/\text{Ti} = 1/4$) and then anchoring the obtained bimetallic alkoxide directly on silica. The last catalyst, having vanadia surrounded by a favourable environment of titania, but anchored directly on silica, have shown lower activities but higher selectivities

with respect to the other two prepared catalysts. This probably means that more uniform catalytic sites can be obtained with the adopted partial hydrolysis procedure. On the other hand, this procedure is much more simple and cheap than the one requiring the previous preparation of a support of silica coated with titania. The grafting procedure could allow, therefore, not only the preparation of the active part, in a well dispersed way, but also the best environment for vanadium oxide in a tailored way, as in the example reported in this paper. All these aspects will be described in the paper in a more detailed way and correlated with the chemical and physical features of the prepared catalysts. These features were determined with the aid of several techniques, such as: BET for the surface area and pore distribution determination, Raman and FTIR, DRIFT spectroscopy for determining the chemical properties of the surface, TPR and O_2 chemisorption for determining redox properties and dispersion of vanadia, XRD for determining the eventual presence of crystalline phases, TEM and SEM for evaluating the structure of the powder. A kinetic approach based on the Mars and Van Krevelen model has initially been applied to all the performed kinetic runs and a pseudo-first order behaviour with respect to propane resulted suitable to interpret the runs.

2. Experimental

2.1. Catalyst preparation

The used support and prepared catalysts are listed in Table 1 together with some their relevant properties. The silica support was supplied by Grace (Type Grace S 432) and calcinated at 773 K for 8 h before the use. The support $\text{TiO}_2/\text{SiO}_2$, used for the

Table 1
Prepared catalyst and supports

Sample	Acronym	TiO_2 (mmol g ⁻¹)	V_2O_5 (wt.%)	S_{SA} (m ² g ⁻¹)
SiO_2	S	–	–	320
$\text{TiO}_2/\text{SiO}_2$	TS	1.41	–	299
$\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$	VTS	1.41	0.8	249
$\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$	V _{hy} TS	1.41	0.9	314
$\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$	V _m TS	0.22	0.8	335

preparation of both VTS and V_{hy} TS catalysts was prepared by grafting titanium isopropoxide (supplied by Fluka) on silica, washing, hydrolysing with steam the residual alkoxide groups, at about 423 K, and finally calcinating at 773 K. The described sequence of operations, namely, grafting, washing, steaming and calcinating were repeated another two times in order to obtain silica coated with a multi-layer of TiO_2 . The adopted procedure and the properties of the used support are described in more details elsewhere [28].

The catalyst VTS was obtained by grafting vanadyl tri-isopropoxide, dissolved in anhydrous *n*-hexane, onto the TiO_2/SiO_2 support by keeping the solution and the solid in contact at room temperature for 24 h under a dry helium atmosphere. The V_{hy} TS catalyst was obtained by grafting partially hydrolysed vanadyl tri-isopropoxide (dissolved in 2-propanol) onto the TiO_2/SiO_2 support, by keeping the solution and the solid in contact, at room temperature for 24 h, under a dry helium atmosphere. Hydrolysis was carried out by dissolving 1 ml of vanadyl tri-isopropoxide in 4 ml of 2-propanol and by adding a stoichiometric amount of water (1:1) containing traces of HCl acting as catalyst. The operation was performed at room temperature, for 5 h, under stirring by placing again the solution under a dry helium atmosphere. The catalyst was recovered by filtration, after the grafting reaction, then washed with the used solvent, dried at 383 K, steamed for 2 h, at 423 K, and finally calcinated at 773 K, for 2 h. The V_m TS catalyst was prepared by grafting a bimetallic vanadium–titanium alkoxide directly onto the SiO_2 support (Grace S 432). The bimetallic alkoxide was obtained by reacting the partially hydrolysed vanadyl tri-isopropoxide (obtained as described for the V_{hy} TS sample) with titanium isopropoxide in a molar ratio 1:4, both dissolved in 2-propanol. The reaction took place at room temperature for 5 h, under stirring and in the presence of a dry helium atmosphere. The obtained solution was used for grafting the bimetallic alkoxide formed, directly on SiO_2 , by operating, at room temperature, for 24 h, under a dry helium atmosphere. The catalyst was recovered by filtration, washed with 2-propanol, steamed at 423 K and calcinated, at 773 K, for 2 h in the usual way. The conditions adopted for preparing the three mentioned catalysts were chosen so that comparable amounts of supported vanadia (0.8–0.9 wt.%) can be obtained, as it can be seen in Table 1.

2.2. Catalysts characterisation techniques

Textural analyses by determining the nitrogen adsorption/desorption isotherms at 77 K were carried out with a ASAP 2010 Micrometrics instrument. Before the analysis, the samples were heated to 623 K under vacuum. Specific surface area S_{SA} and pore dimension distribution were, respectively, determined by BET and BJH methods [29,30].

XRD patterns were recorded on a PW 1877 Philips diffractometer on powdered samples. The scans were collected within the range $5\text{--}60^\circ (2\theta)$ ($0.01^\circ (2\theta) s^{-1}$) using Cu $K\alpha$ radiation.

Raman spectra were obtained using RFS100 Bruker (Nd-Yag line laser resolution on 32 cm^{-1} , power 0.5 W) on calcined samples.

IR spectra were recorded by a Nicolet Avatar 360 instrument, using KBr plates at room temperature for the FTIR. DRIFT analysis has been made at room temperature on samples pre-treated at 400°C under vacuum for 1 h.

TPR profiles were obtained under the following conditions: sample weight 0.3 g, heating rate (from 373 to 873 K) 7 K min^{-1} , flow rate $60\text{ cm}^3\text{ min}^{-1}$, $H_2\text{--}N_2$ 6 vol.%. The sample was treated by flowing air at 653 K for 1 h before the analysis.

The reduced samples were cooled down to 653 K under flow of nitrogen ($60\text{ cm}^3\text{ min}^{-1}$), before the determination of O_2 uptake. Data for O_2 chemisorption were carried out by the pulse technique, using a pulse volume of O_2 (0.15 cm^3) fed over the pre-reduced catalysts. Pulses were repeated until peaks of constant area were obtained from the detector.

SEM observations were made by using a LEO Stereoscan 440. TEM observations were made by using a Jeol Jem 2001 equipped with an EDX probe and sample preparation was as follows: a drop of the dispersion of the milled catalytic powder in isopropyl alcohol was put on a Lacey carbon grid and followed by removal of the dispersant by evaporation at room temperature.

2.3. Catalytic runs

Experimental runs were performed in a pyrex glass cylindrical micro-reactor with a 1 cm internal diameter, at $P = 1\text{ atm}$ and $T = 673\text{--}773\text{ K}$, using a catalyst weight in the range of 0.02–0.04 g. Before the catalytic test, the powdered samples were diluted

Table 2
Details on the packed beds used

	SiO ₂ Grace	VTS	V _{hy} TS	V _m TS
Diluent (SiO ₂ with low <i>S</i> _{SA}) (g)	0.93	0.79	0.81	1.0
Catalyst (g)	0.02	0.03	0.023	0.04
Catalytic bed volume (cm ³)	–	0.78	0.78	1.18
Vanadium (mg)	–	0.13	0.12	0.18

with pure silica with a low specific surface area (7 m² g⁻¹), the diluted powders were then compressed at *P* = 8 atm for 5 min in order to obtain tablets. These tablets were crushed and sieved (37–100 μm). In Table 2 the characteristics of the prepared catalytic bed and catalytic particles are reported. For each catalyst, runs were performed by changing the residence time at three different temperatures: 673, 723 and 773 K. The reaction mixture contained 6.8 vol.% O₂ and 29% (v/v) propane diluted in helium. The flow rates were changed in the range of 10–80 cm³ min⁻¹. Runs in the absence of catalyst were also performed using (i) only the SiO₂ diluent (1 g); (ii) the SiO₂ diluent containing 2.15% (w/w) of SiO₂ Grace S 432.

The reaction products were analysed by gas-chromatography with the same system described in a previous work [31].

3. Results and discussion

3.1. Catalytic activities and selectivities

Activities and selectivities obtained for the different catalysts at three different temperatures (400, 450 and 500 °C) and different residence times, calculated on the overall flow rates, are reported in Table 3. The activity of the inert diluent and silica support could be not negligible at temperature higher than 450 °C. This can be seen in the data reported in Table 4 that has been collected by putting a packed bed of the diluent or of the diluent containing the silica support in the reactor. According to the data, the contribution of the diluent to the activities is less than 3% of propane conversion per gram of diluent, at 500 °C and at the lowest flow rate.

Yields obtained in Figs. 1–3 at different temperatures for VTS, V_{hy}TS and V_mTS catalysts, respectively, are reported as a function of the residence time. In Figs. 4–6, on the contrary, are reported the selectivities to propene as a function of the conversions, for the different catalysts, at 400, 450 and 500 °C, respectively. As it can be seen, the most active catalysts are V_{hy}TS and VTS, while V_mTS is the most selective one. Observed selectivities, at highest temperatures, are further increased when data are corrected for the contribution of the diluent as it can be seen in Table 5, for some runs performed at 500 °C. A rough correlation exists between conversion and selectivity, as it can be seen in Figs. 4–6. Selectivity decreases regularly by increasing conversion. Selectivities are poorly affected by the temperature, as it can be seen in Fig. 7, where all selectivity data against conversion are reported for all the catalysts, at different temperatures and residence times.

A kinetic interpretation of the obtained results has been made. At this scope, some data have been excluded because surely affected by external mass transfer limitation and some others have been excluded too, because oxygen has been completely converted and data are affected by the inert diluent activity contribution. Remaining data have been kinetically interpreted by considering the overall rates of propane conversions:

$$-\frac{d p_{C_3H_8}}{d(W/F)} = \frac{k_1 p_{C_3H_8}}{1 + (k_1/k_0)(p_{C_3H_8}/p_{O_2}^{1/2})} \quad (1)$$

in agreement with the Mars and Van Krevelen model [32].

It is interesting to observe that a pseudo-first order approach, frequently used in the literature [33] is suitable to reproduce our kinetic runs. By submitting kinetic data to mathematical regression analysis it can be noted that the kinetic parameters *k*₁ and *k*₀ resulted strongly correlated. Moreover, their ratio resulted always negligible with respect to 1. It is possible, therefore, to neglect the term at the denominator of relation (1) and the kinetic expression becomes simply:

$$-\frac{d p_{C_3H_8}}{d(W/F)} = k_1 p_{C_3H_8} \quad (2)$$

In Table 6, the results obtained in the simulation of the kinetic runs are reported, together

Table 3
Activities and selectivities for the three catalysts at 400, 450 and 500 °C, varying the contact time

Temperature (°C)	Contact time (s g ⁻¹ cm ⁻³)	Conversion (%)	S _{Propylene} (%)	S _{CO₂} (%)	S _{CO} (%)
VTS					
400	0.02	1.14	65.9	14.6	19.3
	0.04	1.88	58.0	16.1	25.9
	0.06	2.66	50.9	20.2	28.8
	0.18	5.50	40.8	27.1	32.2
450	0.02	3.23	58.5	14.9	26.5
	0.04	4.37	52.1	17.1	30.7
	0.06	6.52	45.9	24.8	37.1
	0.18	9.04	36.0	20.7	43.2
500	0.02	8.04	61.1	25.6	13.1
	0.04	10.91	44.4	16.7	38.8
	0.06	10.64	42.0	17.5	40.4
	0.18	10.43	37.9	17.5	44.5
V _{hy} TS					
400	0.02	1.14	60.4	19.1	20.4
	0.03	1.61	55.5	20.1	24.3
	0.05	2.60	54.0	22.2	23.8
	0.14	4.04	39.8	26.5	33.7
450	0.02	2.66	54.8	18.5	26.3
	0.03	3.70	49.6	19.3	31.1
	0.05	5.38	42.3	21.3	36.3
	0.14	8.78	34.5	22.8	42.7
500	0.02	7.27	48.5	16.1	35.0
	0.03	8.34	44.1	17.7	38.2
	0.05	9.94	41.8	16.2	41.9
	0.14	10.02	40.2	16.3	43.3
V _m TS					
400	0.03	0.29	84.3	14.1	0.6
	0.05	0.63	77.5	14.3	11.8
	0.08	0.86	65.3	17.4	16.9
	0.24	2.16	62.0	24.6	13.3
450	0.03	0.89	73.0	14.2	12.5
	0.05	1.55	68.8	14.1	16.8
	0.08	2.31	63.3	15.5	20.8
	0.24	5.16	51.5	19.4	28.9
500	0.03	3.64	67.3	11.3	20.9
	0.05	3.83	64.3	12.2	23.1
	0.08	7.23	56.5	12.6	30.6
	0.24	10.49	45.0	18.4	36.3

Table 4
Blank runs on diluent and on the silica support

Type of run	Temperature (°C)	Conversion (%)	S _{Propylene} (%)	S _{CO₂} (%)	S _{CO} (%)
Diluent	450	0.76	38	58	4
Diluent	500	2.05	43	39	18
Diluent + SiO ₂ Grace	500	3.5	9	89	2

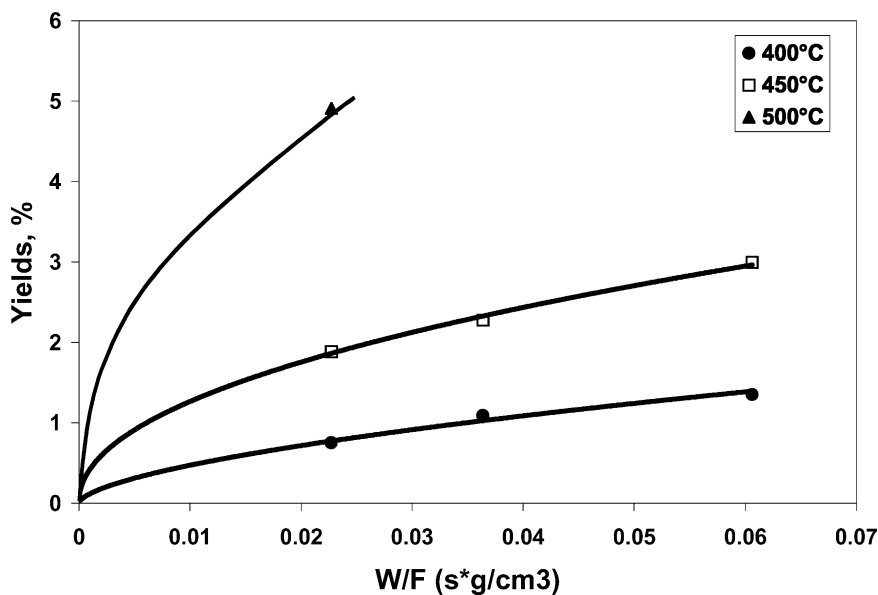


Fig. 1. Yields of propene as a function of residence time, at different temperatures, for the VTS catalyst.

with the kinetic parameters estimated for the best fitting.

That is, for the examined catalysts the hydrogen abstraction from propane seems to be the rate determin-

ing step. Activation energies are about 20 kcal mol^{-1} for all the proven catalysts and the small differences observed in the kinetic parameters reflect the differences of the activities shown by each catalyst.

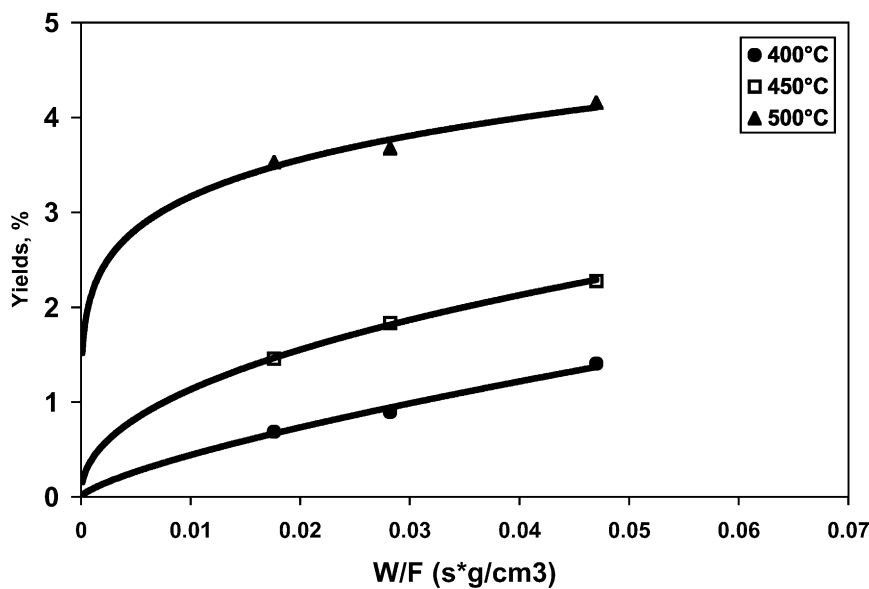


Fig. 2. Yields of propene as a function of the residence time, at different temperatures, for the $V_{hy}TS$ catalyst.

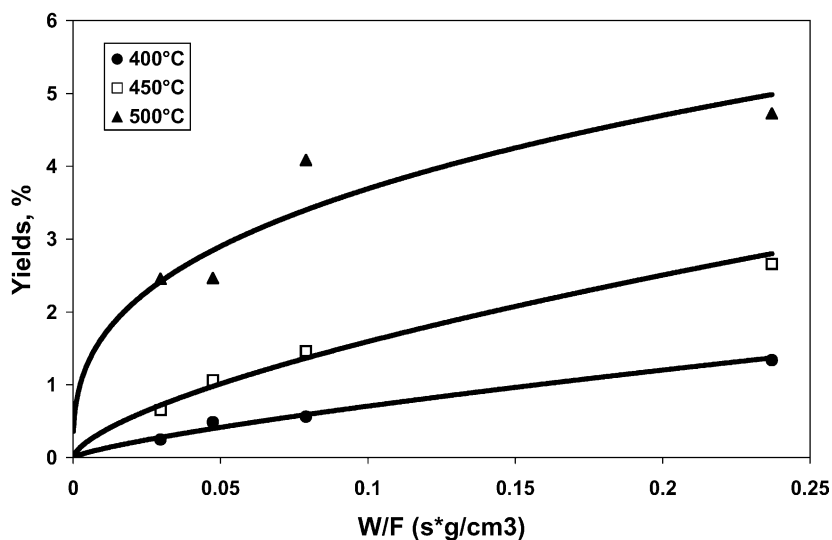


Fig. 3. Yields of propene as a function of the residence time, at different temperatures, for the V_mTS catalyst.

3.2. Catalyst characterisation

3.2.1. Specific surface area, pore distributions

The TiO_2/SiO_2 support was obtained, as before mentioned, by repeating the grafting of titanium tetra-isopropoxide on silica three times. The amount

of titanium supported in any grafting step is reported in Table 7, together with the corresponding specific surface area and the surface hydroxyls density (obtained by TGA as described in a previous work [34]). About a monolayer of TiO_2 was grafted in the first step. Since the hydroxyls density remains

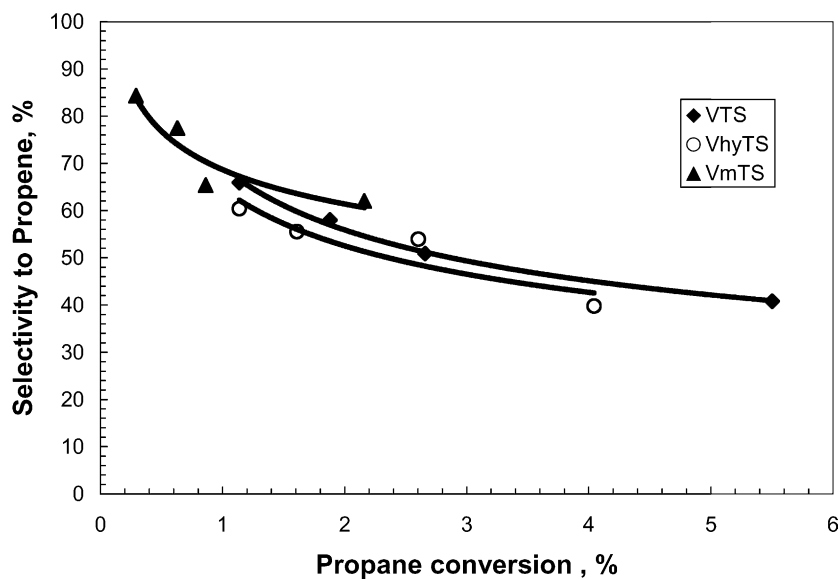


Fig. 4. Selectivity to propene as a function of propane conversion for the three catalysts at 400°C.

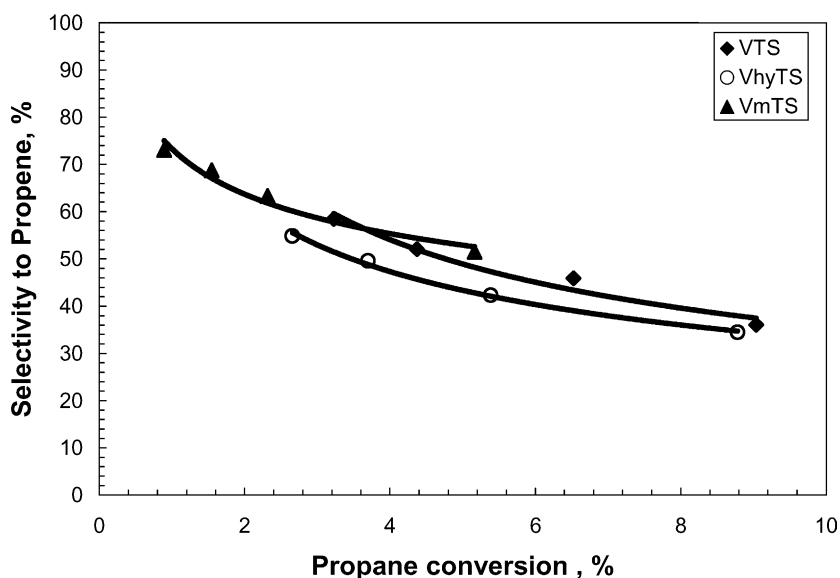
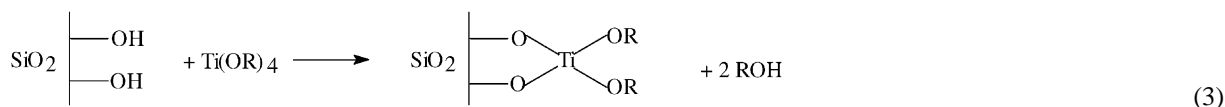


Fig. 5. Selectivity to propene as a function of propane conversion for the three catalysts at 450 °C.

roughly constant after each step of titanium grafting, the reaction probably occurs mainly according to the following stoichiometry:



The specific surface area decreases with the titanium charge during the first grafting step, then it moderately increases until the third grafting step. However, a TiO₂/SiO₂ support with high specific surface area was obtained, which was much higher and more stable than the one obtainable for a pure TiO₂ support. Pores volume and pores distribution are significantly modified for the three grafting steps of titanium alkoxide and

a consistent amount of micropores (20–30%) appears that were not present in the original silica support. The V_mTS catalyst, on the contrary, have maintained both

specific surface area and pore volume close to that of the original silica support.

3.2.2. XRD analyses

The observation of the XRD spectra shows a signal corresponding to the presence of small crystallites of TiO₂ anatase for the TiO₂/SiO₂ support and for VTS and V_{hy}TS catalysts. The sample V_mTS was, on the contrary, completely amorphous. The size of the anatase crystallites seems to be higher in the presence of supported vanadium than in the absence. However, in all cases the amount of amorphous TiO₂ is always largely predominant.

3.2.3. Morphological analyses to SEM, TEM and EDX

The powders observed by SEM showed very singular properties. The silica support showed particles

Table 5

Correction of selectivity, conversion at 500 °C and high contact time considering the diluent effect

Sample	True catalytic conversion (%)	Observed conversion (%)	True selectivity to C ₃ H ₆	Observed selectivity
VTS	7.7	10.4	48.3	37.9
V _{hy} TS	7.2	10.0	52.5	40.2
V _m TS	7.0	10.5	63.9	45.0

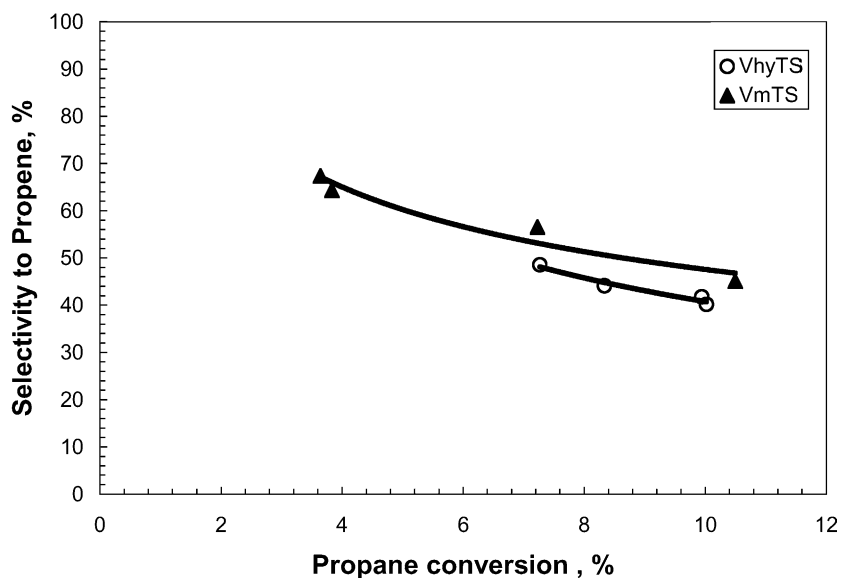


Fig. 6. Selectivity to propene as a function of propane conversion for the three catalysts at 500 °C.

of uniform sizes of about 250 μm . On the other hand, catalysts samples VTS, $V_{\text{hy}}\text{TS}$ and $V_{\text{m}}\text{TS}$ were composed of particles less uniform in size and much smaller. In fact, VTS catalyst had particles falling in the range 2–36 μm , $V_{\text{hy}}\text{TS}$ catalyst had particles falling in the same range, but the presence of very thin particles with a diameter smaller than 1 μm were also detected. $V_{\text{m}}\text{TS}$ catalyst together with the smaller particles having diameter 1–36 μm also showed greater particles of 60–80 μm of diameter. This large change in the particles morphology is probably due to the several sequences of chemical, mechanical and thermal treatments carried out on the original silica support.

TEM observations showed very small crystallites of anatase in samples VTS and $V_{\text{hy}}\text{TS}$ while these were

not present in the sample $V_{\text{m}}\text{TS}$. A semi-quantitative analysis by EDX gave a value of Ti and V of about 10 and 1 wt.% for VTS and $V_{\text{hy}}\text{TS}$, respectively, confirming chemical analysis data. EDX also showed that titanium and vanadium were uniformly dispersed on the surface and that vanadium was never isolated and always bounded to titania, in particular in the catalysts of $V_{\text{m}}\text{TS}$ type. Ti/V aggregates in $V_{\text{m}}\text{TS}$ catalysts cannot be observed also for magnification of 400,000 times being smaller than 10 nm.

3.2.4. Spectroscopic analyses (Raman, FTIR and DRIFT)

Raman spectra were made only on the catalysts VTS and $V_{\text{hy}}\text{TS}$. Since $V_{\text{m}}\text{TS}$ catalyst is completely amorphous and prepared without coating silica surface

Table 6
Kinetic parameters and fitting errors on conversion

Catalyst	Activation energy (kcal mol ⁻¹)	Pre-exponential factor (mol g _{cat} ⁻¹ h ⁻¹ atm ⁻¹)	Mean absolute percent error on propane conversion
VTS	19.9	2.08×10^5	9.8
$V_{\text{hy}}\text{TS}$	18.4	0.81×10^5	10.8
$V_{\text{m}}\text{TS}$	22.2	2.61×10^5	10.7

Table 7
Effect of a TiO₂ grafting on the surface properties of the TiO₂/SiO₂ support

Sample	Grafting step	TiO ₂ (wt.%)	S_{SA} (m ² g ⁻¹)	OH density (μmol m ⁻²)
SiO ₂	0	–	320	2.87
TiO ₂ /SiO ₂	1	5.9	237	2.99
TiO ₂ /SiO ₂	2	9.7	267	2.96
TiO ₂ /SiO ₂	3	11.3	299	2.74

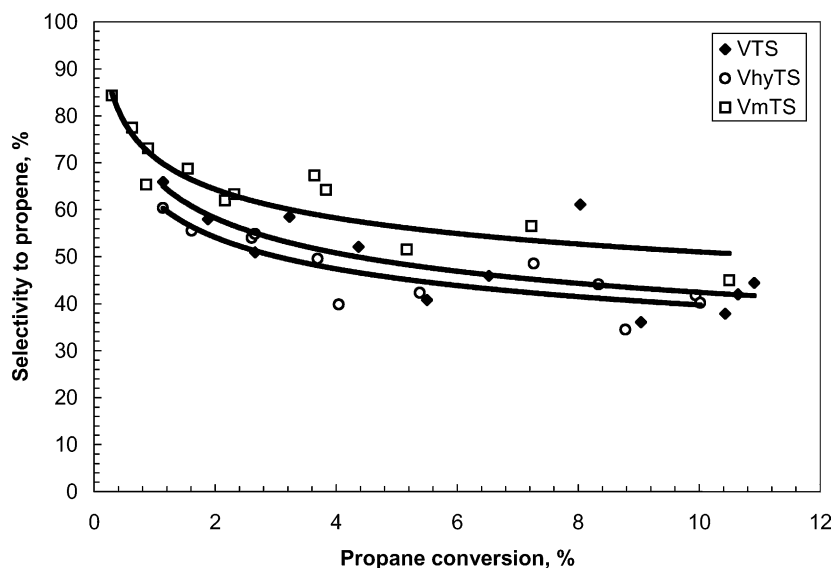


Fig. 7. Selectivity to propene as a function of propane conversion for the three catalysts at different temperatures and residence times.

with a multi-layer of TiO_2 (therefore, does not contain crystallites of anatase) it does not show any band of absorption characteristic of TiO_2 , at the Raman spectroscopy. On the contrary, spectra obtained for VTS and $\text{V}_{\text{hy}}\text{TS}$ showed the presence of absorption bands at 147, 386, 514 and 638 cm^{-1} , respectively, that are typical for anatase. In particular, the signals were well defined for the sample $\text{V}_{\text{hy}}\text{TS}$. A faible absorption appeared at about 1000 cm^{-1} indicating the presence of polyvanadylic agglomerates.

For what concerns FTIR and DRIFT spectra, it must be pointed out, first of all, that in agreement with the XRD analyses, according to which crystalline V_2O_5 is completely absent in all the catalysts, the absorption band, at 1020 cm^{-1} , corresponding to $\text{V}=\text{O}$ vibration and typical of crystalline V_2O_5 , has not been observed. All the other bands, characteristic of V_2O_5 are more or less present together with the bands largely predominant of the used supports. In Fig. 8 DRIFT spectra obtained in the wavenumber range $3450\text{--}3850\text{ cm}^{-1}$ for all the catalysts and related supports are reported. As it can be seen the peak at about 3750 cm^{-1} corresponding to the Si-OH bond vibration are drastically reduced as a consequence of grafting three times titanium alkoxide on silica (see TS spectrum). Catalyst VTS has a spectrum similar to the one of TS, while

$\text{V}_{\text{m}}\text{TS}$ has a spectrum similar to silica, because in this case many residual silanols remains on the surface after grafting the bimetallic alkoxide (Ti-V) precursor on the surface. In Figs. 9 and 10 the DRIFT spectra (wavenumber range $200\text{--}2200\text{ cm}^{-1}$) for SiO_2 , TS, VTS, $\text{V}_{\text{hy}}\text{TS}$ and $\text{V}_{\text{m}}\text{TS}$, respectively, are compared. In this spectra are largely predominant the absorption bands of the supports, that is, the bands characteristic of SiO_2 at 1100 cm^{-1} (asymmetric stretching of the Si-O-Si bonds) and at 800 cm^{-1} (symmetric stretching of the same bonds), the band characteristic of the Si-O-Ti bonds at 970 cm^{-1} . V_2O_5 absorbs mainly in the wavenumber range $550\text{--}670$ and $670\text{--}780\text{ cm}^{-1}$ corresponding to the V-O-V bonds in polyvanadates and in the range $950\text{--}980$ corresponding to the $\text{V}=\text{O}$ vibration in VO_x clusters. The vanadium absorption bands are broad and poorly defined for all the examined catalysts probably as a consequence of the low vanadium loading charge. Moreover, it can be easily recognised that the absorption of $\text{V}_{\text{m}}\text{TS}$ in the wavenumber range $550\text{--}780\text{ cm}^{-1}$ is less pronounced that in the spectra of VTS and $\text{V}_{\text{hy}}\text{TS}$, respectively. This suggests a peculiarity of the $\text{V}_{\text{m}}\text{TS}$ catalyst that seems to have, therefore, more isolated VO_x species probably of the V-O-Ti type, while V-O-V sites are predominant in the other cases.

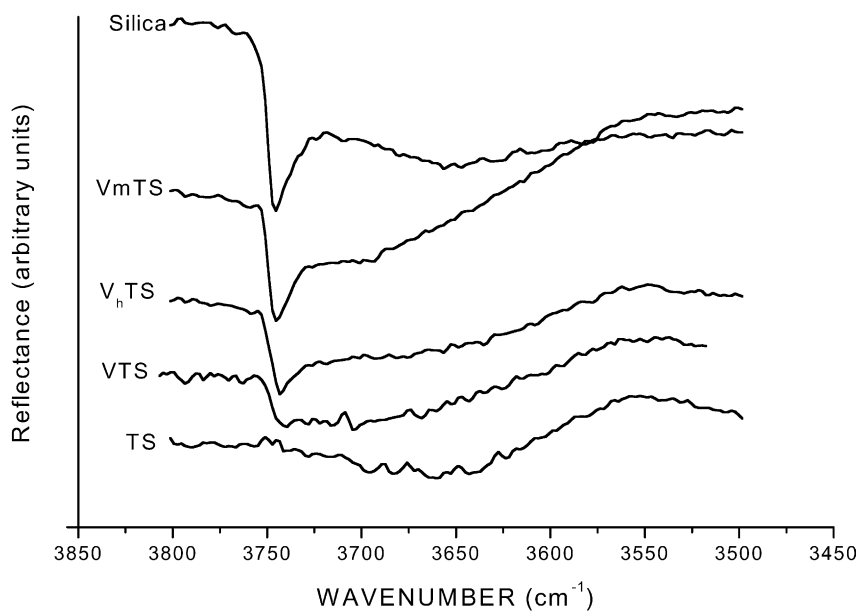


Fig. 8. DRIFT spectra obtained in the wavenumber range 3450–3850 cm⁻¹ for all the catalysts and related support.

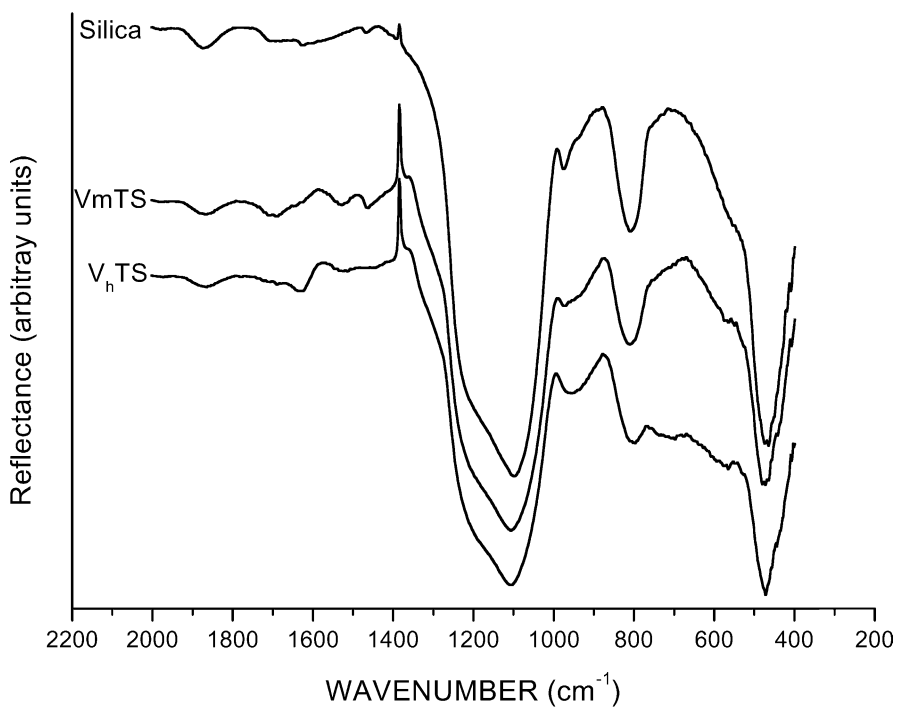


Fig. 9. DRIFT spectra obtained in the wavenumber range 200–2200 cm⁻¹ for silica V_mTS and V_{hy}TS.

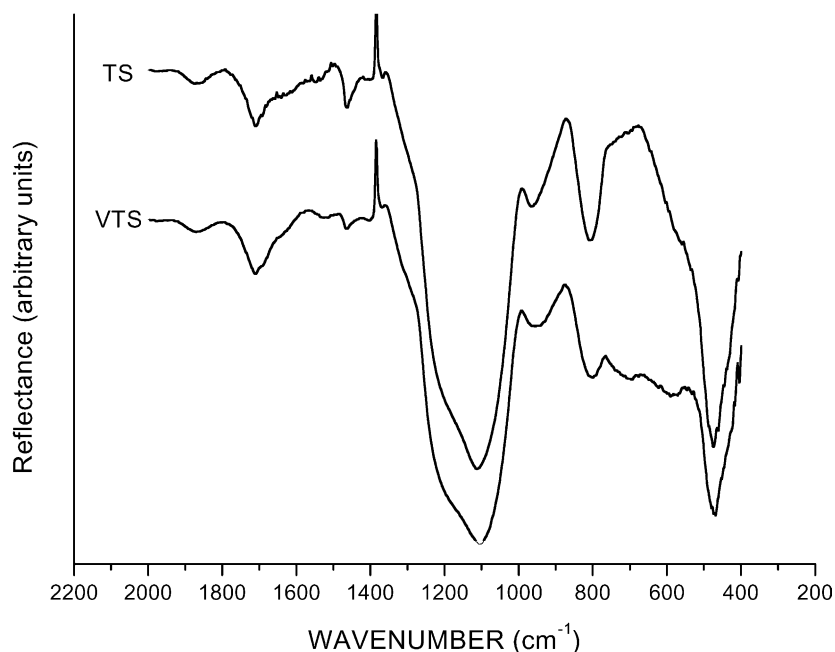


Fig. 10. DRIFT spectra obtained in the wavenumber range 200–2200 cm^{-1} for TS and VTS, respectively.

3.2.5. TPR and oxygen chemisorption by pulse technique

The investigated catalysts showed very different behaviour in the TPR with hydrogen, as can be seen in Fig. 11 reporting the plots related to VTS, $V_{\text{hy}}\text{TS}$ and $V_{\text{m}}\text{TS}$, respectively. All the mentioned catalysts start to be reduced at about 300 °C, but VTS and $V_{\text{hy}}\text{TS}$ show two reducing peaks, one having the maximum at 400 °C and another one at 560 °C. These two peaks probably correspond to catalytic sites of different reducibility and the amount of easily reducible sites are scarce for catalyst VTS compared with $V_{\text{hy}}\text{TS}$. In the case of $V_{\text{m}}\text{TS}$ only one peak at the lower temperature was observed with a narrower distribution of the more reducible sites. This was probably due to the less amount of TiO_2 that was present on its surface. This effect of TiO_2 on the reduction profile has already been observed by Quaranta et al. [35].

On the reduced catalysts, after the adjustment of the temperature at 380 °C, pulses of oxygen were sent on the catalyst. Unreacted oxygen of these pulses was determined by a gas-chromatograph using a HW Detector. It was so possible to evaluate the amount of oxygen retained by the reduced catalysts and to calcu-

late the dispersion of vanadium oxide on the surface. The results obtained are reported in Table 8. From these data it is possible to observe, that the dispersion remains relatively high for all the catalysts, but catalysts prepared by grafting partially hydrolysed vanadyl tri-isopropoxide $V_{\text{hy}}\text{TS}$ and $V_{\text{m}}\text{TS}$ seem to be less dispersed.

Aggregation obtained as a consequence of the mentioned partial hydrolysis of vanadyl tri-isopropoxide and successive reaction with titanium isopropoxide affects the final dispersion and the reducibility of the obtained aggregates. The conclusion is that a moderate aggregation can favour both activity (see, for example, catalyst $V_{\text{hy}}\text{TS}$) and selectivity (see, for example, catalyst $V_{\text{m}}\text{TS}$).

Table 8
Dispersion of vanadium on the prepared catalyst

Catalyst	V_2O_5 (wt.%)	$N_{\text{O}}/10^{18}$ (atm m^{-2})	$Q_{\text{ads}}/V_{\text{supported}}$
VTS	0.8	0.15	0.73
$V_{\text{hy}}\text{TS}$	0.9	0.098	0.62
$V_{\text{m}}\text{TS}$	0.8	0.058	0.45

N_{O} is the density of oxygen atoms referred to the unit of specific area.

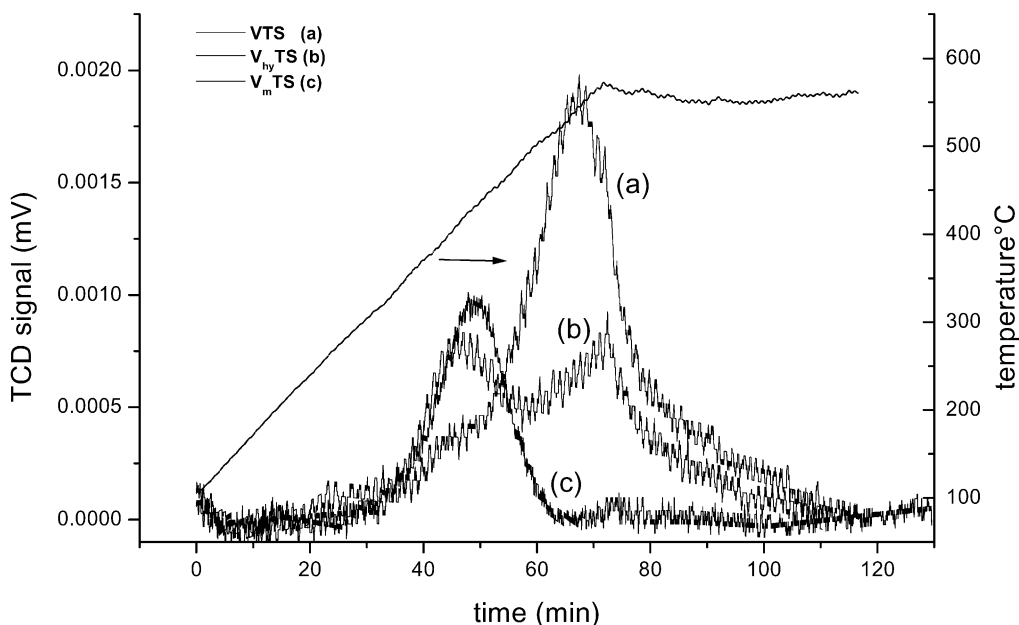


Fig. 11. A comparison of the TPR plots for the three used catalysts.

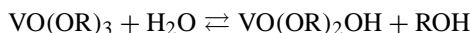
4. Discussion and conclusions

We have seen, first of all, that it is possible to obtain a support of silica coated with a multi-layer of titania by adopting a multistep grafting procedure described both in the present paper and, in more detail, elsewhere [11,28,34]. The obtained support retains the high specific surface area of the original silica but changes completely the chemical properties of the surface, that is characterised by the presence of amorphous TiO_2 , together with very small crystallites of anatase. Vanadyl tri-isopropoxide strongly interacts with the hydroxyls of TiO_2 and can easily be anchored to this support. It seems to favour, after grafting, the formation and growth of TiO_2 crystallites. However, amorphous TiO_2 remains largely predominant. The different grafting steps and successive catalyst treatments largely change the morphology of the obtained powders, as observed with the SEM microscopy. However, the specific surface area and pore distributions are less affected. VTS catalyst shows the lowest specific surface area. This is probably due to the fact that vanadyl tri-isopropoxide, dissolved in *n*-hexane, can enter the pores of the support by occluding some of

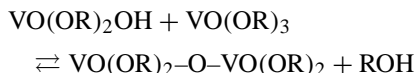
them. This occurs with less probability for $\text{V}_{\text{hy}}\text{TS}$ and $\text{V}_{\text{m}}\text{TS}$ catalyst, as a consequence of the condensations reactions, occurring as a consequence of the partial hydrolysis of vanadyl tri-isopropoxide, dissolved in isopropanol and treated with small amounts of water, giving place to bulky molecules. These observations together with the observed changes of the powder morphology and the occurring surface reaction stoichiometry, can explain the moderate increase of the specific surface area observed for the two last mentioned catalysts.

Before discussing about the obtained kinetic results it is useful to interpret what, probably, happens when the different catalysts are prepared by grafting vanadyl tri-isopropoxide dissolved in *n*-hexane. The structure of this alkoxide, that is liquid, is not well known. However, it is reasonable to assume a dimeric structure similar to the one ascertained for the vanadyl trimethoxide dissolved in CCl_4 [36] or monomeric as for vanadyl tri-isobutoxide [37]. $\text{V}_{\text{hy}}\text{TS}$ has been prepared by hydrolyzing vanadyl tri-isopropoxide dissolved in isopropanol with a stoichiometric amount of water ($\text{V}/\text{H}_2\text{O} = 1$) containing small amount of HCl for catalysing the reaction. The hydrolysis occurs

as it follows:

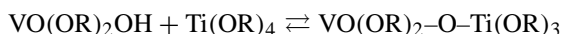


This reaction is then followed by condensation reactions of the type



All these reactions are contrasted by the large excess of isopropanol used as solvent, the molecular weight of the oligomers formed remains, therefore, relatively low and linear oligomers prevail. The catalyst obtained by grafting these oligomers remains well dispersed, because almost all the vanadium atoms are accessible, despite the occurred condensation.

Catalyst $V_m\text{TS}$ has been prepared by hydrolyzing vanadyl tri-isopropoxide as for $V_{\text{hy}}\text{TS}$ catalyst and adding then titanium isopropoxide in a molar ratio $V/\text{Ti} = 1/4$. Some different reactions can occur in this case, giving place to condensation products of the type:



or products of aggregation such as



This last reaction can also occurs with the oligomeric species of vanadium. All these species are then grafted directly on silica (S) and not on titanium coated silica (TS), as in the previous cases.

As titanium alkoxide is present in a large amount in the solution with respect to vanadium and has a great affinity for the silica support, grafting occurs essentially giving place to Si–O–Ti bonds. Vanadium follows titanium during the grafting remaining bonded to it. This last catalyst has, therefore, the peculiarity of a large number of V–O–Ti or V=O terminal sites with respect to the other two catalysts where more V–O–V sites are present. This is also confirmed by the DRIFT analysis. These sites are also more uniform and more easily reducible as it arises from the TPR analysis. This peculiarity of the $V_m\text{TS}$ catalyst is probably responsible of the greater selectivity obtained in the ODH of propane.

The kinetic behaviour of the examined catalysts is quite similar. In all cases the hydrogen abstraction

from the hydrocarbon seems to be rate determining step and the reaction occurs with a pseudo-first order kinetic law showing an activation energy of about 20 kcal mol^{-1} .

By concluding we have seen that the preparation of redox catalysts using the grafting procedure can determine interesting improvements in the performances of the catalysts by individuating and preparing the most suitable precursor to be grafted.

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