Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 118 (2006) 298–306

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The characterization of the V species and the identification of the promoting effect of dopants in V/Ti/O catalysts for *o*-xylene oxidation

F. Cavani [a,*], C. Cortelli [a], A. Frattini [a], B. Panzacchi [a], V. Ravaglia [a], F. Trifirò [a],
C. Fumagalli [b], R. Leanza [b], G. Mazzoni [b]

[a] *Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna, Italy*[1]
[b] *Lonza, Via E. Fermi 51, 24020 Scanzorosciate (BG), Italy*

Abstract

The present work deals with the study of the role of promoters in TiO_2-supported vanadium oxide, catalyst for the oxidation of *o*-xylene to phthalic anhydride. Two different series of catalysts were prepared, the first one consisting of undoped samples having different vanadium oxide content, and the second one of samples having 7 wt.% V_2O_5 and variable amounts of Sb and Cs as promoters. All the samples were characterized by means of Raman spectroscopy, X-ray diffraction and thermal-programmed reduction and oxidation, in order to define a method for the quantification of the different V species (i.e., isolated vanadium, dispersed polyvanadate and bulk vanadium oxide) that develop on TiO_2 support in the presence of promoters. It was found that polyvanadate and bulk vanadium oxide spontaneously release molecular oxygen at 600–650 °C, whereas the isolated V is not susceptible of self-reduction. The latter species is predominant in samples having low vanadium oxide loading ($\leq$2 wt.% V_2O_5, with TiO_2 surface area 22.5 m^2/g), and possesses the highest intrinsic activity in *o*-xylene conversion. The presence of Sb, a promoter of activity, increases the dispersion of the most active species and also hinders its segregation in the reaction environment. These promoting effects are more pronounced when both Cs and Sb are present.

Keywords: Vanadium oxide; Titanium oxide; Selective oxidation; o-Xylene; Phthalic anhydride; Antimony oxide; Cesium oxide

1. Introduction

Supported vanadium oxide is used as the catalyst for several oxidation reactions. One of the most important example is the V_2O_5/TiO_2 system (V/Ti/O) for *o*-xylene oxidation to phthalic anhydride [1–6]. Actually, the industrial system is more complex since it includes several dopants, the nature and the relative amount of which vary depending on catalyst supplier and on the technology employed for the process, either a single-bed or a multi-layer catalytic fixed-bed. The promoters included in catalyst formulation have a remarkable effect on both, activity and selectivity to phthalic anhydride [3–8].

The V/Ti/O system has been the object of several investigations [9,10]; in most cases the aim of the work was to characterize the different vanadium species that develop at the TiO_2 surface. It is known that the interaction between vanadium oxide and TiO_2 generates: (i) a V species, which is chemically bound to the support via oxo bridges (isolated V in octahedral or tetrahedral coordination, depending on the hydration degree), (ii) a polymeric species, spread over titanium oxide and (iii) bulk vanadium oxide, either amorphous or crystalline. Moreover, relationships have been looked for between the characteristics of each V species and the catalytic performance in *o*-xylene oxidation. However, the quantification of these different vanadium species is a difficult task and all the techniques employed (e.g., potentiometric titration after dissolution of the samples [11], deconvolution of Raman bands [12], O_2 chemiadsorption [13], NO and NH_3 chemiadsorption [14], UV–vis–DRS [15] and XPS [16], to cite a few), may lead to uncertain attributions in the presence of dopants or with high vanadium oxide loading, that are the typical features of industrial catalysts for *o*-xylene oxidation.

Despite the well-known importance of promoters, there are few works dealing with the study of doped V/Ti/O catalysts

---

* Corresponding author.
E-mail address: fabrizio.cavani@unibo.it (F. Cavani).

[1] INSTM, Research Unit of Bologna. A Partner of Concorde CA and of Idecat NoE (6FP of the EU).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.07.016

[17–20]. Promoters have been classified as belonging to either the non-interacting-elements class (WO_3, Nb_2O_5, SiO_2; the former two are present in V/Ti/O systems for SCR, while the latter is often present as an impurity in the raw materials rather than being intentionally added), which coordinate directly to the support and do not significantly interact with V oxide, or to the interacting-elements class (K_2O and P_2O_5), which coordinate with the V ion and thus may profoundly affect the redox property of the latter [9,17,21]. In general, one problem in the study of doped V/Ti/O catalysts is that the promoting elements are usually added in very small amounts (much lower than the vanadium oxide), and therefore the identification of physical–chemical differences due to their addition may become particularly difficult.

In a recent work [18], we have characterized Cs-doped V/Ti/O systems by means of TPR and TPR + O (re-oxidation after TPR), together with conventional spectroscopic methods. This allowed us to give an interpretation to the activity-enhancement effect observed when small amounts of Cs are added to a 7 wt.% V_2O_5-containing V/Ti/O catalyst. A relationship was found between V re-oxidation (the rate-determining step of the redox process for the Cs-doped catalyst), and catalytic activity of samples containing increasing amounts of Cs. The experimentation also led us to conclude that the thermal characterization methods employed can be used to directly discriminate the different V species, while isolating the effects of promoters. In the present work, we extend this investigation approach to both the undoped and doped V/Ti/O systems, the latter containing two important promoters for the industrial catalyst, Cs and Sb.

2. Experimental

Catalysts were prepared by the wet impregnation technique: an aqueous solution containing the desired amount of NH_4VO_3, $CsNO_3$ and $Sb(CH_3COO)_3$ was added to the support (TiO_2 anatase, having a specific surface area of 22.5 m^2/g). Water was evaporated under mild evacuation at 70 °C. Then the wet solid was dried at 150 °C for 3 h, and calcined at 450 °C for 5 h in static air.

The composition of the samples prepared is summarized in Table 1. Two samples series were studied: the first one containing only vanadium oxide (Vx, with an amount ranging from 1 to 15 wt.% V_2O_5, with respect to the overall weight of the sample), and the second one with a fixed amount of vanadium (7 wt.% V_2O_5), and a variable amount of the two promoters. The support surface area and the amount of the different elements were chosen so to prepare industrial-like samples.

Table 1
Samples prepared and their composition

Sample, code	V_2O_5 (wt.%)	Cs_2O (wt.%)	Sb_2O_3 (wt.%)
V1	1	–	–
V2	2	–	–
V3.5	3.5	–	–
V5	5	–	–
V7	7	–	–
V10	10	–	–
V15	15	–	–
Cs0.35	7	0.35	
Sb0.7	7	–	0.7
Cs0.35Sb0.35	7	0.35	0.35
Cs0.35Sb0.7	7	0.35	0.7
Cs0.35Sb3.5	7	0.35	3.5

The catalysts prepared were characterized by means of X-ray diffraction, Raman spectroscopy, thermal-programmed reduction (TPR) and oxidation (TPO, and TPR + O for the oxidation after pre-reduction). The XRD diffraction patterns were taken using a Philips PW 1710 apparatus, with Cu Kα (λ = 1.5406 nm) as radiation source. Raman studies were performed using a Renishaw 1000 instrument, equipped with a Leica DMLM microscope, laser source Argon ion (514 nm). Thermal-programmed measurements were performed using a Thermoquest TPDRO1100 instrument. Calcined samples, shaped in 250–590 μm granules, were loaded in a quartz reactor and pre-treated in nitrogen at 150 °C for 30 min to eliminate weakly adsorbed species. After cooling at room temperature, N_2 was replaced by the analyzing gas (5% H_2 in Argon for TPR tests, 5% O_2 in He for TPO), and the temperature was linearly increased up to 650 °C (thermal ramp: 10 °C/min); the samples were finally maintained at 650 °C for 30 min. In TPR + O tests, the samples were first reduced, and then were re-oxidized following the TPO protocol.

Catalytic tests were carried out in a laboratory continuous-flow, fixed-bed reactor. The size of the catalyst particles ranged from 250 to 590 μm. The feed composition was 1 mol.% *o*-xylene in air. The products in the outlet stream were condensed in acetone. The reactants and the products were analyzed with a GC equipped with a HP-5 semicapillary column (FID) for organic compounds and with a Carbosieve S column (TCD) for O_2, CO and CO_2. Catalytic results were obtained after the catalyst had been equilibrated, that is after approximately 20–30 h reaction

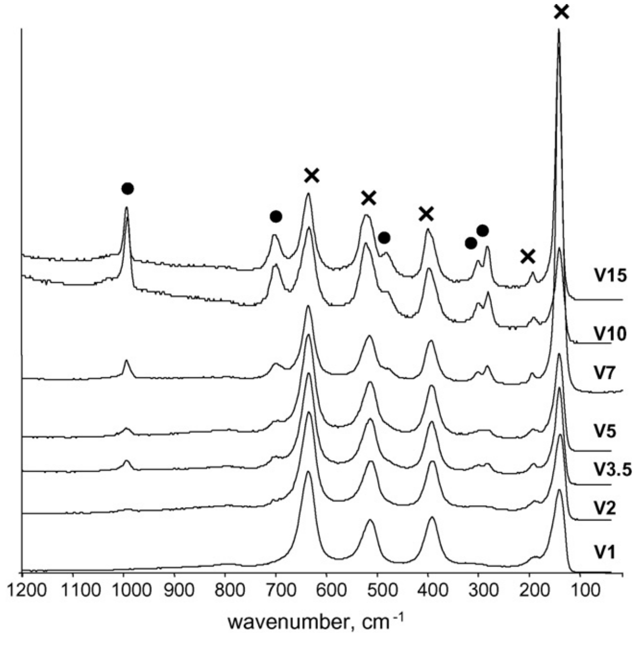

Fig. 1. Raman spectra of Vx samples: ((×) TiO_2 rutile and (●) V_2O_5).

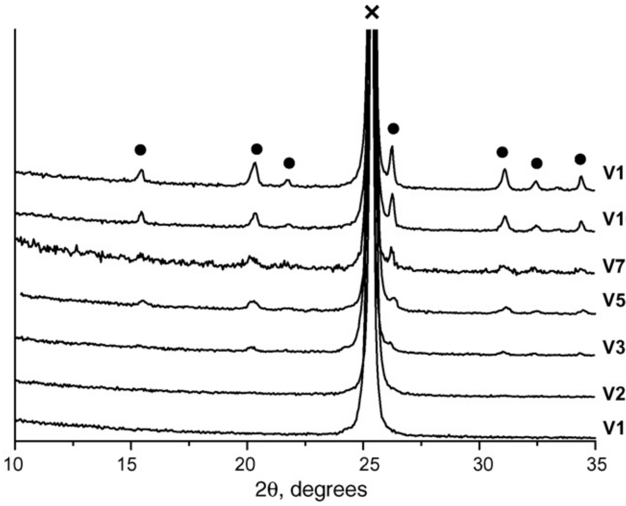

Fig. 2. XRD patterns of V*x* samples: ((×) TiO_2 rutile and (●) V_2O_5).

time; after this equilibration step, the catalysts had a quite stable catalytic performance.

3. Results and discussion

3.1. Characterization and reactivity of undoped V/Ti/O catalysts

Unpromoted calcined V*x* samples were characterized by Raman spectroscopy (Fig. 1) and X-ray diffraction (Fig. 2); from both techniques, it was possible to exclude the presence of bulk vanadium oxide (amorphous or crystalline) in the samples having vanadium oxide content lower than 3.5 wt.% V_2O_5 (i.e., in V1 and V2 samples). In fact, the Raman bands attributable to bulk V_2O_5 (at 998, 705, 483, 305 and 285 cm^{-1}), and the corresponding XRD reflections, were observed only in those samples having an overall vanadium oxide content higher than 2 wt.%. It is worth mentioning that a mixture prepared by grinding together 1 wt.% V_2O_5 with TiO_2 led to a sample having a Raman spectrum and a XRD pattern in which the bands and reflections, respectively, relative to bulk vanadium oxide were clearly visible. This means that in samples V1 and V2 the absence of features belonging to V_2O_5 is due to the spreading of this compound on TiO_2, and not to a detection sensitivity limit of the techniques employed. This also agrees with all literature indications concerning the development of isolated V species and bi-dimensional structures for low contents of the active phase [1–6].

The ‘‘monolayer’’ coverage of vanadium oxide over TiO_2 is reached for 7.9 atoms/nm^2 [22], comparable to the value of alumina and zirconia. Isolated V species $O{=}V(O{-}Ti)_3$ possess a Raman band at 1030–1035 cm^{-1}, associated to the vanadyl stretching; this band, however, is visible only in dehydrated samples [23]. The band becomes very broad upon exposure to moisture, due to extensive solvation of the VO_4 units [10,24]. This is the reason why in spectra of our samples no feature relative to dispersed V species was evident.

We tried to determine the relative amounts of the different V species by reduction in programmed temperature (TPR), since each species is characterized by a different reducibility, and hence by a defined reduction peak in a TPR profile [12,25,26]. In Fig. 3(left), the reduction profile of sample V5 is shown, together with the result of the de-convolution procedure, when the contributions relative to the three different species are assigned [18,19,25,26]: (i) at ≈500 °C, for isolated V species, which is the more easily reducible, (ii) at 550 °C for polyvanadates and (iii) at 600 °C for bulk vanadium oxide, either amorphous or crystalline. It is evident that the complexity of the profile does not allow a reliable assignment of the relative contribution of each peak, and that the de-convolution of the experimental peak may suffer from a large degree of uncertainty.

Only in the case of samples having very low vanadium oxide content, e.g., in V1 and V2, the use of TPR information is possible without uncertainty. In fact, in these samples a single reduction peak was observed in the low temperature range (Fig. 3(right)), which indicated the exclusive presence of isolated, easily reducible V species. An additional problem in the use of TPR for the quantification of the different V species arises in presence of dopants, which are themselves susceptible of reduction; for instance, the reduction of Sb in doped V/Ti/O

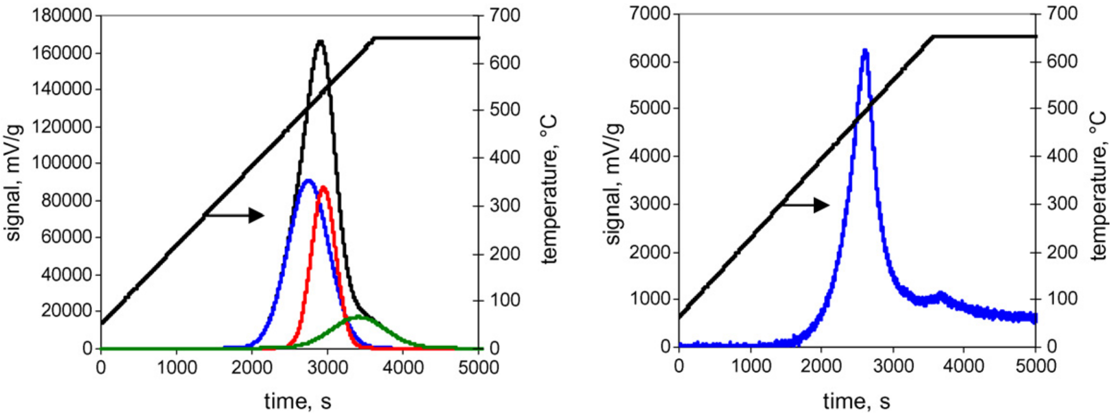

Fig. 3. *Left*: TPR profile of V5 and de-convolution into three reduction peaks. *Right*: TPR profile of V2.

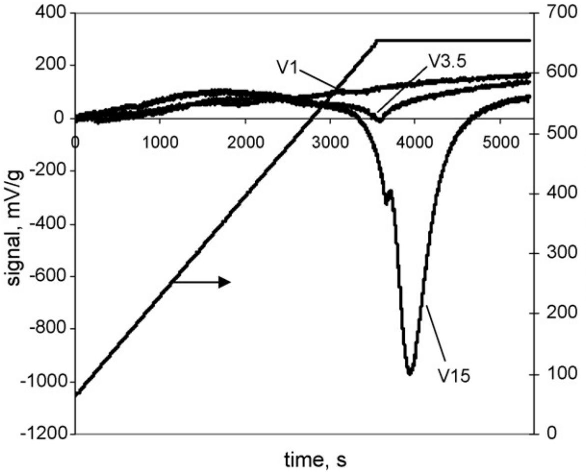

Fig. 4. TPO profiles of selected Vx samples.

samples occurs at a temperature similar to that of isolated V or polyvanadate [27,28].

In order to overcome the problem of the uncertainty and the arbitrariness in de-convolution of TPR profiles, we have used an alternative approach to discriminate between the different V species in undoped and in doped samples, by means of direct oxidation in programmed temperature (TPO). In fact, we have reported in a previous work [18] that TiO_2-supported vanadium oxide spontaneously releases molecular oxygen at 650 °C under oxidizing atmosphere (5% O_2 in He), while antimony oxide, and obviously Cesium oxide as well, are not susceptible of self-reduction. Fig. 4 shows the TPO profiles of a few samples; they exhibited very small oxygen consumption (corresponding to positive peaks in the profiles), indicating that V was in its highest oxidation state, or that it was eventually stabilized in a reduced state [29]. At 650 °C, during the final isothermal step, samples V3.5–V15 showed a negative peak, due to the release of molecular oxygen; this did not occur in the case of V1 and V2 samples.

The spontaneous release of oxygen is due to the formation of VO_2 or of thermodynamically more stable vanadium suboxides, the Magneli phases. It is known that bulk V_2O_5 spontaneously self-reduces to V_6O_{13} at temperatures higher than 550 °C, when low partial pressures of oxygen are present in the gas phase [30,31]. However, with bulk vanadium oxide the loss of O_2 does not occur in the presence of air (as we also experimentally confirmed), while it does occur even under these conditions when vanadium oxide is supported over TiO_2. This is likely related to the presence of a specific crystallographic fit between vanadium oxide and TiO_2 [2] that modifies the thermodynamic parameters of the former oxide as compared to bulk, unsupported V_2O_5. Also, it is likely that the reduction of vanadium oxide is accompanied by the migration of reduced V species into the bulk of TiO_2, as a consequence of the transformation of the latter from the polymorph anatase into the more stable rutile form [32]. This transformation is known to be favoured in the presence of vanadium oxide [1–3]. Indeed, when we carried out a second TPO experiment with our samples, neither a low-temperature O_2 consumption, nor high-temperature O_2 release were experimentally found; this confirms that V ions had been stabilized by dissolution in the TiO_2 matrix. The formation of rutile was confirmed by characterization with Raman spectroscopy and X-ray diffraction of samples after the TPO measurement.

The TPO profiles of samples indicate that isolated vanadium, the only species in V1 and V2, does not release O_2. Therefore, the TPO profile can be used for the quantitative discrimination of this species from polyvanadate and bulk vanadium oxide. Table 2 reports the amount of isolated V and of vanadium oxide which underwent spontaneous self-reduction (polyvanadate + bulk vanadium oxide), as evaluated from the quantitative determination of the molar quantity of O_2 released; the latter is plotted in molar ratio with V in Fig. 5, as a function of the overall vanadium oxide loading. It is shown that the molar ratio approaches the theoretical value for the reduction of V_2O_5 to V_6O_{13} (0.167). This supports the hypothesis that under the conditions used for TPO tests, polyvanadate and bulk vanadium oxide release O_2 with the formation of this mixed-valence oxide. Therefore, when this ratio is equal to ≈0.17, all the V present in the sample self-reduces to V_6O_{13}, and this means that the sample does not contain isolated V.

Data in Table 2 indicate that V3.5 and V5 possessed both V species, while samples having the highest loading (V10 and V15), did not possess isolated V at all. These data agree with literature indications; when the vanadium oxide loading is increased, the formation of dispersed polyvanadate is preferred over that of isolated V [1,12,21].

Samples were tested as catalysts for the oxidation of *o*-xylene to phthalic anhydride. Fig. 6 summarizes the catalytic activity: the temperature at which 60% *o*-xylene conversion

Table 2
Amount of vanadium species in Vx samples, as evaluated from TPO tests

Sample	Isolated V species		Polyvanadate + bulk vanadium oxide	
	Relative amount[a] (%)	Absolute amount, (mmol/g_{cat})	Relative amount[a] (%)	Absolute amount, (mmol/g_{cat})
V1	100	0.11	0	0
V2	100	0.22	0	0
V3.5	66	0.25	34	0.13
V5	55	0.30	45	0.25
V7	4	0.03	96	0.73
V10	0	0.00	100	1.07
V15	0	0.00	100	1.58

[a] With respect to the overall V content.

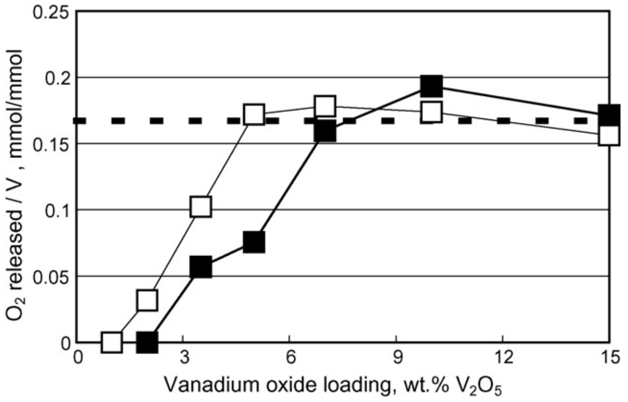

Fig. 5. Molar ratio between the amount of O_2 released and the V content in samples V1–V15, as a function of vanadium oxide loading, calculated from TPO (■) and TPR + O (□) tests. Dotted line corresponds to the stoichiometric reduction of V_2O_5 to V_6O_{13}.

was reached is plotted as a function of vanadium oxide loading. The more active was the catalyst, the lower was the temperature necessary to reach a defined level of conversion. V1 and V2 were the most active, despite the very low vanadium oxide content; V3.5 was the least active. Therefore, a drastic fall of activity occurred when the vanadium oxide content was increased from 2 to 3.5 wt.%. Thereafter, for a loading higher than 3.5 wt.%, the activity of samples increased again, but nevertheless remained lower than that of sample V2.

The same figure also reports the absolute amount of the isolated V species and of polyvanadate + bulk vanadium oxide as evaluated from TPO profiles (Table 2). In the case of samples V1 and V2, those having exclusively isolated V, a relationship is evident between the amount of this species and the activity, while in the case of samples Vx having $x \geq 3.5$ the activity increased for $3.5 \leq x \leq 7$ and then remained approximately constant for $x > 7$. These data suggest that:

(a) The isolated V was the species characterized by the highest activity in the transformation of *o*-xylene. Recently, it was reported that monomeric vanadyl (V═O) is the most active species in the selective oxidation of toluene to benzoic acid, and that this species is responsible for the catalytic activity of V/Ti/O in this reaction [33].

(b) The development of polyvanadate and bulk vanadium oxide (as inferred from Raman spectra and XRD patterns), starting from sample V3.5, caused the activity of isolated V to be repressed. Indeed, in V3.5 the amount of isolated V was comparable to that of V2, but its activity was much lower. This indicates that polyvanadates may in part build overlayers, covering the isolated V species and limiting its contribution to catalytic performance.

(c) From V3.5 onwards ($3.5 \leq x \leq 15$ in Vx), the catalytic performance was mainly determined by the amount of polyvanadate. Polyvanadate is known to be more active than V in bulk vanadium oxide [1], but the latter species was likely predominant in V10 and V15; this led to the levelling off of activity in these samples.

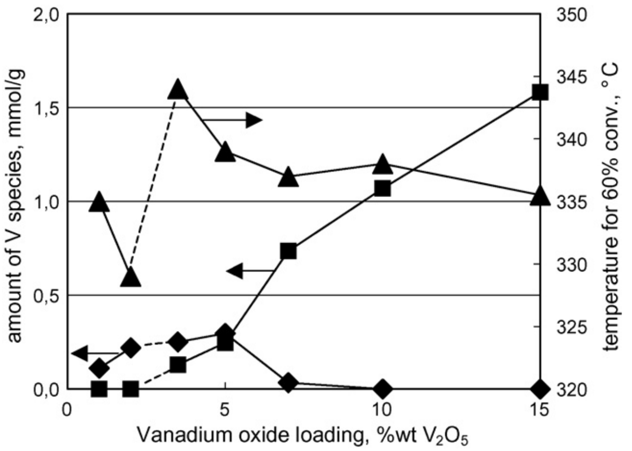

Fig. 6. Effect of vanadium oxide loading in Vx samples on the temperature at which 60% *o*-xylene conversion is reached (residence time 0.25 s) (▲), the absolute amount of isolated V species (◆) and the absolute amount of polyvanadate + bulk vanadium oxide (■).

Fig. 7 reports the effect of temperature on *o*-xylene conversion and on the distribution of products for V1 (top) and V15 (bottom); these catalysts had comparable activity (Fig. 6). The selectivity to phthalic anhydride increased when the reaction temperature was increased, due to the transformation of the reaction intermediates (phthalide, *o*-tolualdheyde and *o*-toluic acid) to the final product [34,35]. The selectivity to

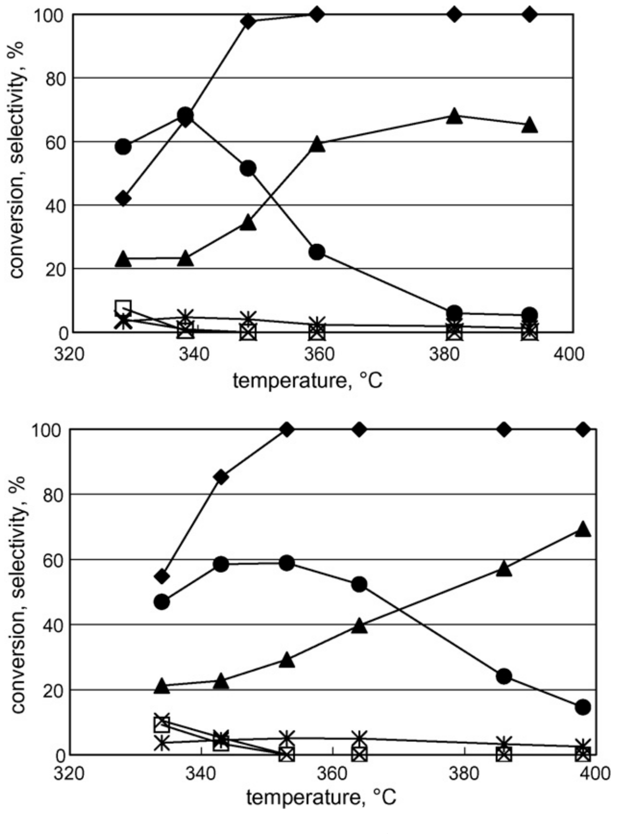

Fig. 7. Catalytic activity of V1 (top) and V15 (bottom). Symbol: *o*-xylene conversion (◆); selectivity to phthalic anhydride (●), COx (▲), phthalide (□), *o*-toluic acid plus *o*-tolualdehyde (×) and benzoic acid plus maleic anhydride (*), residence time 0.25 s.

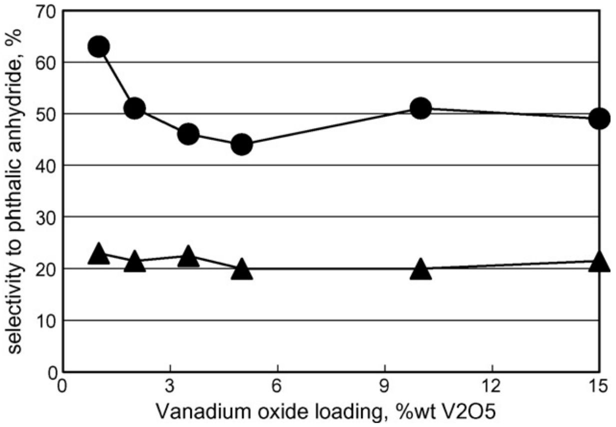

Fig. 8. Selectivity to phthalic anhydride (●) and CO*x* (▲) at 60% *o*-xylene conversion, residence time 0.25 s.

CO*x*, benzoic acid and maleic anhydride also increased, due to the oxidative degradation reactions, which preferably occurred at high temperature. V1 reached the higher maximum selectivity to phthalic anhydride (69% versus 60% for V15); however, in the former case, the maximum selectivity to phthalic anhydride was obtained at 340 °C, for an *o*-xylene conversion of 67%. On the contrary, V15 maintained the maximum selectivity to phthalic anhydride up to total *o*-xylene conversion. As a consequence of this, the fall of selectivity to phthalic anhydride and the corresponding increase of selectivity to CO*x* were steeper with V1 than with V15.

Fig. 8 compares the selectivity to phthalic anhydride and to CO_x at 60% *o*-xylene conversion, as a function of the overall vanadium oxide loading. It is shown that the selectivity to phthalic anhydride first decreased in the 1–5 wt % V_2O_5 range, and then slightly increased for a further increase of active phase loading. Samples having intermediate vanadium oxide content, V3.5 and V5, the catalytic performance of which was mainly controlled by the polyvanadate species, were the least selective to phthalic anhydride. The lower selectivity was due neither to the formation of CO*x* (which was almost independent on V content), nor to the selectivity to intermediate oxidized products, but to the formation of phthalic acid.

3.2. Characterization of the undoped samples after reduction (TPR tests) and after o-xylene oxidation

Even when the pre-reduced samples were re-oxidized (TPR + O tests), the oxidation profile showed a negative peak, after the positive peaks due to O_2 consumed for V re-oxidation; in some cases, however, the amount of O_2 released was greater than that released during TPO tests. Fig. 5 compares the molar ratio between the amount of O_2 released and V as a function of the vanadium oxide content in catalysts, for both TPO and TPR + O tests. The greater difference between TPO and TPR + O was with V2, V3.5 and V5, while with samples having either less (V1) or more (V7, V10 and V15) vanadium oxide, the amount of oxygen released was similar in the two cases. This suggests that the pre-reduction induced changes in the distribution of the different V species; the isolated V was not stable, and the reduction cycle led to a segregation of part of it into polymeric species or bulk vanadium oxide. Moreover, this also indicates that the pre-reduction did not cause the transformation of anatase into rutile and the migration of vanadium into the rutile lattice. This was confirmed by Raman and XRD spectra of samples after the TPR measurements; no evidence was obtained for the formation of rutile.

Undoped samples were characterized by means of TPO after *o*-xylene oxidation. Fig. 9 compares the oxidation profiles of fresh and spent V5 and V10. Changes in the TPO profiles are evident; in spent catalysts, the peak relative to O_2 release was shifted towards lower temperature with respect to the corresponding fresh samples. However, while in the case of fresh V10 the overall amount of oxygen released per unit weight was only 1.6 times the corresponding amount in the spent sample, in the case of spent V5 the intensity of the peak was clearly much higher than that of the fresh one; this is in agreement with the results of TPO and TPR + O tests (Fig. 5). In catalysts having the higher vanadium oxide amount, the reaction atmosphere only caused a modification of the characteristics of the O_2-releasing V species, since these catalysts did not contain isolated V at all. On the contrary, in the case of V5 the reaction environment caused a segregation of the isolated V with generation of the O_2-releasing V species.

Moreover, in spent catalysts the shift of the peak associated to O_2 release towards lower temperatures indicates that the nature of the interaction of polyvanadate and bulk vanadium

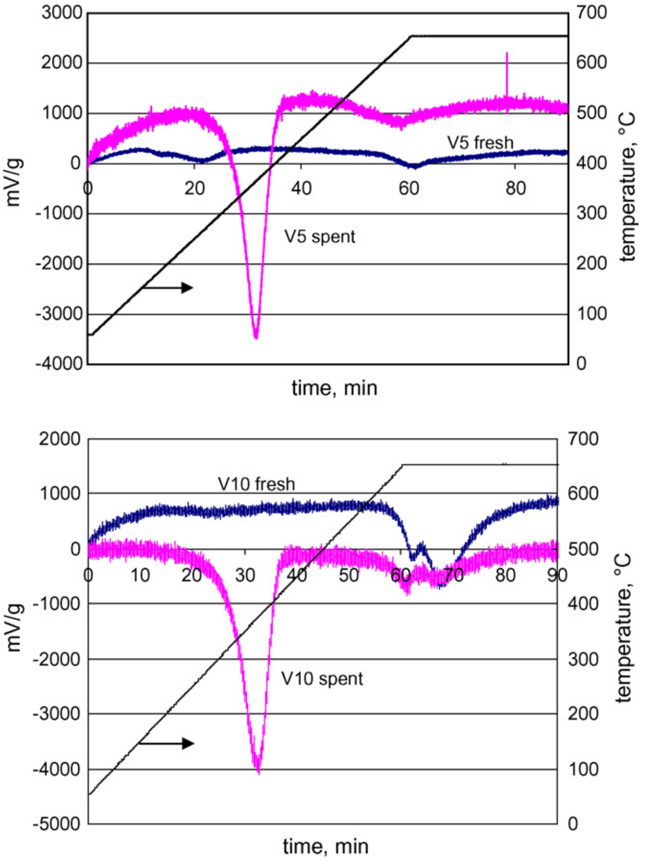

Fig. 9. TPO profiles of fresh and V5 (top) and V10 (bottom).

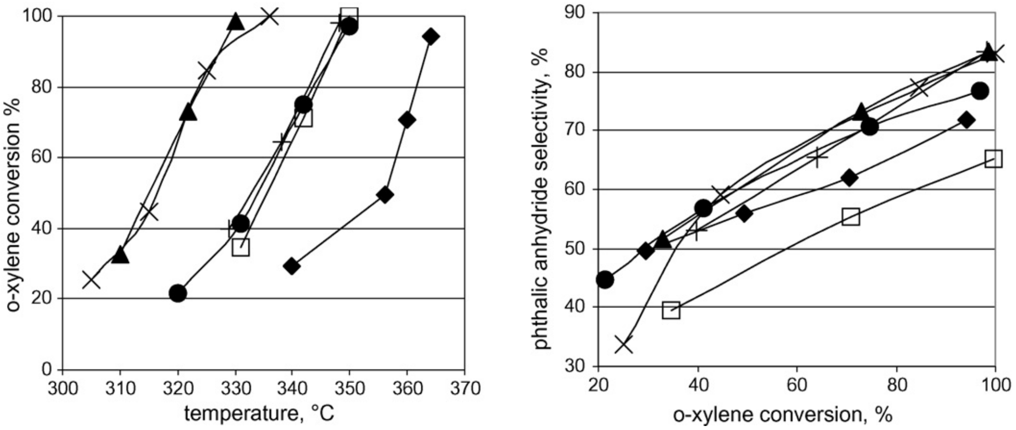

Fig. 10. *Left*: Conversion of *o*-xylene as a function of temperature. *Right*: Selectivity to phthalic anhydride as a function of *o*-xylene conversion. Catalysts: V7 (◆), Sb0.7 (□), Cs0.35 (●), Cs0.35Sb0.7 (▲), Cs0.35Sb0.35 (×) and Cs0.35Sb3.5 (+), residence time 0.13 s.

oxide with TiO_2 was modified as a consequence of the reaction environment.

The following are the main conclusions concerning undoped V/Ti/O systems:

1. By TPO, it is possible to calculate the amount of isolated V and of polyvanadate + bulk vanadium oxide;
2. The isolated V is the most active species in the oxidation of *o*-xylene to phthalic anhydride;
3. The preferential formation of polyvanadate and bulk vanadium oxide leads to less active catalysts;
4. The selectivity to phthalic anhydride is affected by the presence of the different V species, but differences are not dramatic; the most important effect are on the formation of phthalic acid and on the selectivity to phthalic anhydride at high temperature;
5. The isolated V is not stable, and during the reduction step in TPR measurements a great part of it segregates into polyvanadates or bulk vanadium oxide, especially in those samples having higher vanadium oxide content (>2 wt.% V_2O_5);
6. A modification of the nature of V species also occurs during reaction.

3.3. *Characterization and reactivity of Sb-, Cs- and Cs/Sb-doped V/Ti/O catalysts: role of promoters*

The addition of Sb or Cs, or the combination of both, greatly affected the catalytic performance of V/Ti/O catalysts. Fig. 10(left) compares the conversion of *o*-xylene as a function of temperature for the doped samples; all catalysts contained 7 wt.% V_2O_5 (see Table 1 for compositions). The presence of either Sb or Cs promoted the catalytic activity, but when both Sb and Cs were present, the activity increase was even more pronounced. It is worth noting that Cs contents higher than 0.35 wt.% Cs_2O in Cs-doped samples [18] and Sb contents higher than 0.7 wt.% Sb_2O_3 in Sb-doped samples had a negative effect on catalytic performance. Therefore, it is evident that there is a synergic promotional effect of the two elements in samples Cs0.35Sb0.7 and Cs0.35Sb0.35.

The promoting effect of Cs on catalytic activity was studied in a previous work [18]. It was found that the presence of Cs modifies the rate-determining step of the redox process; the addition of Cs decreased V reducibility, but improved V re-oxidizability. Therefore, one effect of Cs on activity was related to the acceleration of V re-oxidation rate.

Fig. 10(right) reports the trend of selectivity to phthalic anhydride as a function of *o*-xylene conversion for the doped samples. Cs0.35 was more selective than V7, while Sb0.7 was the least selective of all catalysts investigated. It is known that Cs is a promoter for both activity and selectivity [18], while the negative effect of Sb on selectivity is unexpected and in disagreement with literature dealing with the role of this element in V/Ti/O catalysts [19,28]. This indicates that the method for dopant addition in V/Ti/O and its amount in relation to that of vanadium oxide are crucial parameters that affect its role. Indeed, industrial patents dealing with the catalyst composition in multi-bed reactors claim Sb as a promoter in the finishing section, i.e., in the part of the catalytic bed aimed at the combustion of traces of unconverted *o*-xylene, although at the expense of the selectivity to phthalic anhydride [7,8]. This seems to support the view of Sb as a promoter of activity, rather than of selectivity. However, data of Fig. 10 demonstrate that the simultaneous presence of both Cs and Sb greatly improved the catalytic performance; in this case the catalyst was more active and more selective than the undoped one, V7.

Table 3 compares the molar ratio between O_2 released and V, as evaluated from negative peaks in TPO and TPR + O profiles,

Table 3
Molar ratio between O_2 released and V, and amount of isolated V species in doped samples as evaluated from TPR + O and TPO tests

Sample	O_2 released/V (mmol/mmol)	Isolated V, by TPR + O[a] (%)	Isolated V, by TPO[a] (%)
V7	0.1648	0	4
Sb0.7	0.1521	12	nd
Cs0.35Sb3.5	0.1508	12	nd
Cs0.35Sb0.35	0.1370	20	nd
Cs0.35Sb0.7	0.1361	21	28

[a] Relative amount, with respect to the overall V content.

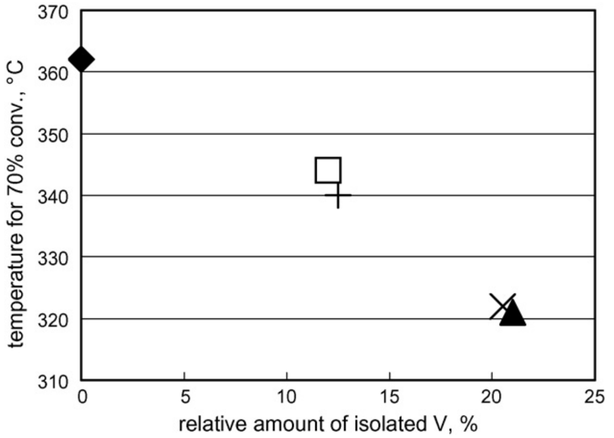

Fig. 11. Temperature for 70% *o*-xylene conversion as a function of the relative amount of isolated V species, as evaluated from TPR+O tests, in different undoped (V7) and doped samples containing 7 wt.% V_2O_5: V7 (◆), Sb0.7 (□), Cs0.35Sb0.7 (▲), Cs0.35Sb0.35 (×) and Cs0.35Sb3.5 (+).

and the corresponding amount of isolated V. The presence of the promoters increased the amount of isolated V, for the same overall vanadium oxide content (7 wt.% V_2O_5). The greater effect was obtained with samples containing both Cs and Sb, when Sb was present in low quantity (Cs0.35Sb0.35 and Cs0.35Sb0.7). In these catalysts, the amount of isolated V was comparable to the maximum one in V*x* samples, that is the amount obtained with V3.5. An excessive amount of Sb (i.e., in Cs0.35Sb3.5) was instead detrimental, because the number of isolated V sites decreased with respect to samples having lower promoter quantity. Furthermore, it is likely that in this case the development of bulk antimony oxide led to the coverage of the active sites [28].

Fig. 11 summarizes the results of catalytic tests; the temperature for 70% *o*-xylene conversion is plotted as a function of the relative amount of isolated V, for both undoped and doped V/Ti/O samples containing 7 wt.% V_2O_5. A relationship is evident, which confirms that the isolated V species mainly determines the conversion of *o*-xylene; the role of promoters was to increase the relative amount of this species.

Furthermore, the presence of promoters stabilized isolated V, and avoided its segregation during the pre-reduction treatment in TPR + O tests. This is evident from Table 4, that compares the amount of this species for Cs0.35Sb0.7, as calculated from TPR + O and TPO profiles; only a slight decrease of it occurred during the pre-reduction in TPR + O tests (from 28 to 21%). In the case of V5 and V7 samples, instead, the pre-reduction treatment led to the segregation of the whole fraction of isolated V species.

Table 4
Isolated V species, as evaluated from TPO and TPR + O tests

Sample	Isolated V, by TPO[a] (%)	Isolated V, by TPR + O[a] (%)
V5	55	0
V7	4	0
Cs0.35Sb0.7	28	21

[a] Relative amount, with respect to the overall V content.

The higher amount of isolated V species in doped samples may be due to a direct interaction of promoters with VO_4 units. For instance, it has been reported that alkali and alkaline earth metals have a high affinity for vanadium, and tend to readily complex V species; in such a way, the formation of crystalline V_2O_5 particles is delayed until vanadium oxide ‘‘titrates’’ these elements [10,17,36]. Furthermore, the speciation of supported oxides is known to depend on the PZC of the surface [37]; the development of a more basic support surface as a consequence of Cs or Sb oxide addition may favour the formation of monomeric vanadate species.

4. Conclusions

The chemical–physical features and the catalytic performance of undoped and doped V/Ti/O, catalyst for the selective oxidation of *o*-xylene to phthalic anhydride, were compared. It was found that it is possible to discriminate between isolated vanadium and polyvanadate + bulk vanadium oxide by means of TPO measurements. In fact, bulk vanadium oxide and polyvanadate release oxygen during oxidation, whereas the isolated vanadium does not.

In undoped V/Ti/O samples, isolated vanadium was present only for low amount of vanadium oxide (<5 wt.% V_2O_5); moreover, this species was the only one in samples having a vanadium oxide loading lower then 3.5 wt.% V_2O_5. Catalytic tests and characterization of fresh and spent samples evidenced that the isolated vanadium is the most active species in *o*-xylene conversion, but that also it is not stable under a reductive atmosphere and under reaction conditions as well. The addition of a suitable amount of Sb and Cs in V/Ti/O made possible to develop a higher amount of isolated vanadium, with a correspondingly lower quantity of polyvanadate and bulk vanadium oxide, as compared to the undoped samples. This led to a considerable increase of catalytic activity.

References

[1] G. Centi, Appl. Catal. A 147 (1996) 267.
[2] P. Courtine, E. Bordes, Appl. Catal. A 157 (1997) 45.
[3] B. Grzybowska, Appl. Catal. A 157 (1997) 263.
[4] C.R. Dias, M.F. Portela, G.C. Bond, Catal. Rev.—Sci. Eng. 39 (3) (1997) 169.
[5] V. Nikolov, D. Klissurski, A. Anastasov, Catal. Rev.—Sci. Eng. 33 (1991) 319.
[6] G.C. Bond, Appl. Catal. A 191 (2000) 69.
[7] P. Reuter, G. Voit, T. Heidemann, WO Patent 0216299 (2003), assigned to BASF AG.
[8] M. Okuno, T. Takahashi, European Patent 1063222 (2000), assigned to Nippon Catalytic Chem. Ind.
[9] J.C. Vedrine, in: J.C. Vedrine (Ed.), Catal. Today 20 (1994) (Eurocat Oxide).
[10] I.E. Wachs, B.M. Weckhuysen, Appl. Catal. A 157 (1997) 67.
[11] E. Garcin, R. Surantyn, A. Chambosse, A. Foucault, G. Coudurier, J.C. Volta, J.Ph. Nogier, A.M. De Kersabiec, F. Cavani, J. Van Ommen, B. Grzybowska, M. Czervenka, K. Malec, A. Andersson, Catal. Today 20 (1994) 23.
[12] G.T. Went, L.J. Leu, A.T. Bell, J. Catal. 134 (1992) 479.
[13] K. Chary, G. Kishan, T. Bhaskar, C. Sivaraj, J. Phys. Chem. B 102 (1998) 6792.

[14] M. Inomata, K. Mori, A. Miyamoto, Y. Murakami, J. Phys. Chem. 87 (1983) 754.
[15] X. Gao, I.E. Wachs, J. Phys. Chem. B 104 (2000) 1261.
[16] G.C. Bond, J.P. Zurita, S. Flamerz, Appl. Catal. 27 (1986) 353.
[17] G. Deo, I.E. Wachs, J. Catal. 146 (1994) 335.
[18] S. Anniballi, F. Cavani, A. Guerrini, B. Panzacchi, F. Trifirò, C. Fumagalli, R. Leanza, G. Mazzoni, Catal. Today 78 (2003) 117.
[19] U.A. Schubert, F. Anderle, J. Spengler, J. Zuehlke, H.J. Eberle, R.K. Grasselli, H. Knoezinger, Topics Catal. 15 (2001) 195.
[20] M.G. Nobbenhuis, P. Hug, T. Mallat, A. Baiker, Appl. Catal. A 108 (1994) 241.
[21] B. Grzybowska, Topics Catal. 21 (2002) 35.
[22] I.E. Wachs, Catal. Today 27 (1996) 437.
[23] X. Gao, S.R. Bare, J.L.G. Fierro, I.E. Wachs, J. Phys. Chem. B 103 (1999) 618.
[24] J.-M. Jehng, G. Deo, B.M. Wechkuysen, I.E. Wachs, J. Mol. Catal. A 110 (1996) 41.
[25] S. Besselmann, C. Freitag, O. Hinrichsen, M. Muhler, Phys. Chem. Chem. Phys. 3 (2001) 4633.
[26] D.A. Bulushev, L. Kiwi-Minsker, F. Rainone, A. Renken, J. Catal. 205 (2002) 115.
[27] B. Pillep, P. Behrens, U.A. Schubert, J. Spengler, H. Knoezinger, J. Phys. Chem. B 103 (1999) 9595.
[28] J. Spengler, F. Anderle, E. Bosch, R.K. Grasselli, B. Pillep, P. Beherens, O.B. Lapina, A.A. Shubin, H.J. Eberle, H. Knoeziger, J. Phys. Chem. B 105 (2001) 10772.
[29] F. Cavani, E. Foresti, F. Trifirò, G. Busca, J. Catal. 106 (1987) 251.
[30] K. Devriendt, H. Poelman, L. Fiermans, Surf. Sci. 433 (1999) 734.
[31] J. Haber, M. Witko, R. Tokarz, Appl. Catal. A 157 (1997) 3.
[32] G. Deo, Private communication, in occasion of the 5th Group Symposium, May 2005.
[33] C. Freitag, S. Besselmann, E. Löffler, W. Grünert, F. Rosowski, M. Muhler, Catal. Today 91–92 (2004) 143.
[34] G.C. Bond, J. Catal. 116 (1989) 531.
[35] R.Y. Saleh, I.E. Wachs, Appl. Catal. 37 (1987) 87.
[36] M. Sanati, L.R. Wallenberg, A. Andersson, S. Jansen, Y. Tu, J. Catal. 132 (1991) 128.
[37] G. Deo, I.E. Wachs, J. Phys. Chem. 95 (1991) 5889.