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The catalytic performance of Cs-doped V/Ti/O catalysts in the oxidation of *o*-xylene to phthalic anhydride: a TPR/TPO and reactivity study

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Abstract

Titania-supported vanadia (V/Ti/O) systems were modified by addition of cesium oxide for application as catalysts in the selective oxidation of *o*-xylene to phthalic anhydride (PA). Catalytic tests demonstrated that cesium is a strong promoter of the activity and selectivity to PA, but this effect is evident only under well-defined reaction conditions. Samples with a Cs content lower than 0.35 wt.% Cs_2O exhibited a considerable increase in conversion as compared with the undoped V/Ti/O system. Catalytic tests made with varying *o*-xylene and oxygen concentrations in the feed demonstrated that in Cs-doped V/Ti/O catalysts the rate-determining step is the re-oxidation of vanadium by molecular oxygen. Thermal-programmed reduction (TPR) and thermal-programmed re-oxidation (TPO) tests evidenced that the addition of Cs decreases the vanadium reducibility and increases the re-oxidizability of the reduced vanadium sites. The positive effect of Cs on selectivity to PA was evident only for *o*-xylene concentrations in feed lower than 1.5 mol%.

Keywords: *o*-Xylene oxidation; Phthalic anhydride; Vanadium oxide; V/Ti/O catalyst; Cesium oxide; Promoter effect

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1. Introduction

One of the most important industrial applications of catalysts based on titania-supported V_2O_5 is the selective oxidation of *o*-xylene to phthalic anhydride (PA). The titania-supported vanadia (V/Ti/O) system is doped with alkali metal ions (e.g. potassium or cesium), phosphorus, and transition or post-transition elements such as molybdenum and antimony in order to enhance the catalytic performance in terms of activity and selectivity to the desired product as well as to increase the catalyst lifetime [1–3]. A large number of patents claim the importance of dopants, which often are present in large amounts, and which may considerably affect the reactivity of vanadium. Despite the industrial importance of this multi-component system, also used for SCR of No_x and studied as the catalyst for several different oxidation reactions (e.g. oxidation of methanol, toluene, and butadiene), relatively few papers have appeared in the literature where the role of dopants is systematically studied [4–10]. Indeed the majority of papers deal with the nature of the interaction between titania and vanadium oxide and the nature of the V species in the reference system V/Ti/O, analyzing the role of the main chemical–physical features of titania [11,12 and references therein].

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Deo and Wachs [8] have studied the effect of the main dopants in V/Ti/O systems as reported in the literature, and have classified the additives 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 thus 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. Concerning the specific effect of alkali metal ion additives on the catalytic performance of V/Ti/O in selective oxidations, sometimes the results reported in the literature differ considerably, since the method of catalyst preparation, the amount of dopant and the way it is added may affect the catalyst features and reactivity. It is generally believed that alkali metal ions titrate the surface acid sites, and that they promote the selectivity to PA by increasing the overall catalyst basicity. This behavior in principle should favor the desorption of electron-richer molecules and avoid their consecutive combustion. However, no experimental evidence is reported to support this general belief. Moreover, it was found that potassium may form bronzes or KVO_3 by reaction with vanadium, and decreases the V reducibility, with a corresponding decrease in catalyst activity and sometimes, an increase in the selectivity to the product of partial oxidation [4–7].

Even though cesium is claimed in all industrial patents as one of the main promoters in catalysts for *o*-xylene oxidation [2, see for example [13]], no systematic study has ever been published on the effect of this promoter on catalytic performance and on the chemical–physical features of the catalysts. The aim of the work reported here was to study the effect of Cs on a V/Ti/O-based system, catalyst for the selective oxidation of *o*-xylene to PA.

2. Experimental

Catalysts were prepared by the wet-impregnation technique: the support was TiO_2 in the anatase crystalline form, with a BET surface area of $22\,m^2/g$. An aqueous solution of ammonium vanadate (Sigma) and cesium nitrate (Aldrich) was prepared, containing the two salts in the desired relative amounts. The titania was dropped into the solution, and the solvent was evaporated at 70 °C in a rotavapor. The powder obtained was then dried and calcined for 3 h at 150 °C, followed by heating to 450 °C for 5 h in air. Samples were prepared containing 7 wt.% V_2O_5 and increasing amounts of Cs.

The X-ray diffraction (XRD) measurements were carried out using a Philips PW 1710 apparatus, with Cu Kα ($\lambda = 1.5406$ nm) as the radiation source. Thermal-programmed reduction (TPR) and thermal-programmed re-oxidation (TPO) tests were carried out using a Termoquest TPDRO instrument. The reducing and oxidizing gases were composed of 5% (v/v) H_2 in Ar and 5% (v/v) O_2 in He, respectively: 0.1 g of each calcined sample, shaped in 250–590 μm granules, were loaded in a quartz glass reactor, and first heated in an N_2 flow at 120 °C for 1 h to eliminate weakly adsorbed water. After cooling to room temperature, the nitrogen was replaced by the reducing gas (TPR measurement) and the linear temperature program was started: 10 °C/min from room temperature up to 650 °C followed by the final isothermal step of 30 min at 650 °C. The temperature of the catalytic bed was detected by a thermocouple. The outlet gas from the reactor was analyzed with a TCD detector. After the reducing step, the catalysts were cooled and subjected to a re-oxidation treatment (TPO measurement), using the same temperature program.

Catalytic tests were carried out in a conventional continuous-flow, fixed-bed, stainless steel reactor, working at atmospheric pressure. The feed composition was 1.0 mol% of *o*-xylene in air. The total flow (F) was $45\,cm^3$/min and the amount of the catalyst (W) was 0.25 g, which resulted in a contact time of 0.3 s. The size of the catalyst particles ranged from 250 to 590 μm (unless otherwise specified). The products in the outlet stream were first condensed, and the residual gaseous flow was scrubbed in acetone. Reactants and products were analyzed with a GC equipped with a HP-5 capillary column (FID) for condensable products and with a Carbosieve S column (TCD) for oxygen and carbon oxides. Particular care was devoted to determination of the C balance, which was found always to fall between 95 and 105% (calculated as the comparison between converted *o*-xylene and the sum of the product yields).

Table 1
Samples prepared, and their composition

Samples	Cs_2O (wt.%)	V/Cs atomic ratio
Cs0	0	∞
Cs0.1	0.1	108
Cs0.35	0.35	31
Cs0.5	0.5	22
Cs0.8	0.8	14
Cs1.0	1.0	11

3. Results and discussion

3.1. Reactivity in o-xylene oxidation

Table 1 gives the list of samples prepared (all of them contained 7 wt.% V_2O_5), the amount of Cs and the atomic ratio between V and Cs for each sample. The surface area of all samples was the same as that of the reference titania, i.e. 22 m^2/g. In the text, the samples are referred to on the basis of their Cs content (e.g. Cs*x*).

Fig. 1 reports the XRD patterns of the samples. Besides the reflections of TiO_2 (anatase) and the weak reflections attributable to crystalline V_2O_5, there also are weak lines which have been attributed to $Cs_2V_6O_{16}$. These weak $Cs_2V_6O_{16}$ reflections are the only evidence for Cs doping and are clearly present only in the Cs1.0 sample, where the atomic ratio between V and Cs is equal to 11.

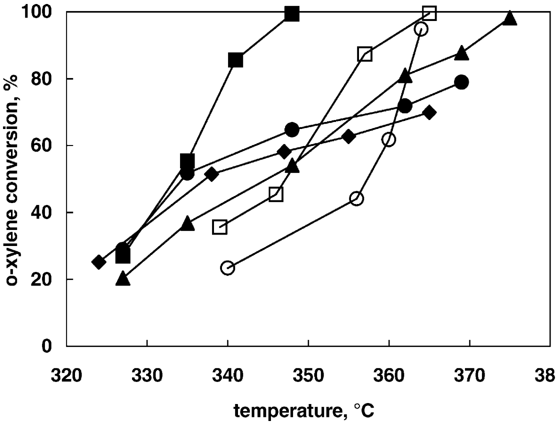

Fig. 2. Conversion of *o*-xylene as a function of temperature for the samples: Cs0 (○); Cs0.1 (□); Cs0.35 (■); Cs0.5 (▲); Cs0.8 (●); Cs1.0 (◆). Feed: 1.0% *o*-xylene in air, residence time 0.3 s.

Fig. 2 reports the effect of the reaction temperature on the *o*-xylene conversion, for each sample. The results are also summarized in Fig. 3 where the temperatures of 30 and of 70% *o*-xylene conversion are plotted as functions of the Cs content in the samples. The effect of Cs on activity was remarkable. An increase in Cs led to a considerable increase in catalytic

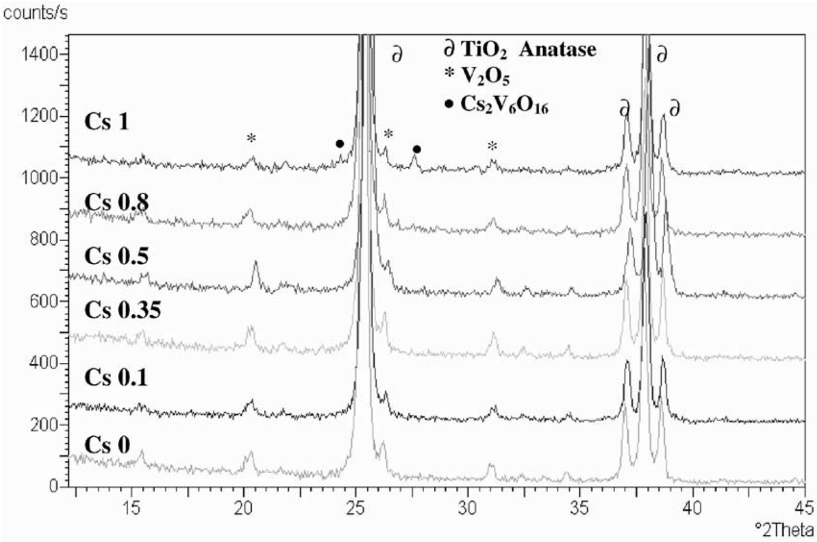

Fig. 1. XRD patterns of calcined samples.

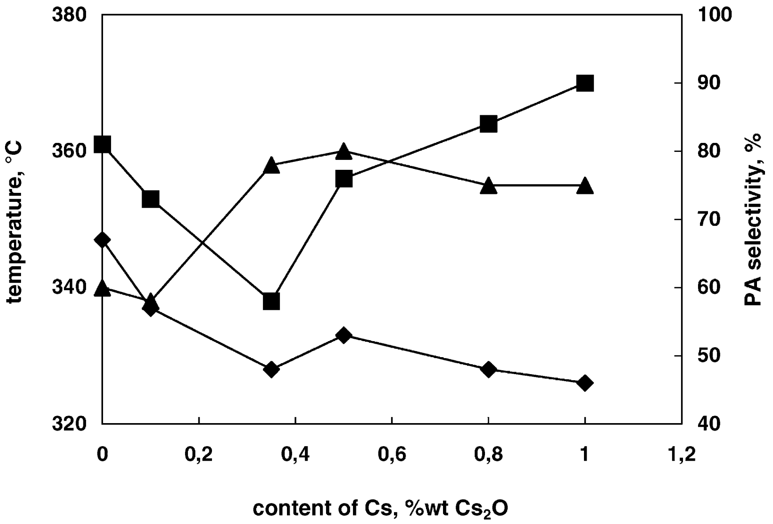

Fig. 3. Temperature of 30% (◆) and 70% (■) *o*-xylene conversion and selectivity to PA (▲) at 70% *o*-xylene conversion as functions of the content of Cs in the samples. Conditions as in Fig. 2.

activity, as shown by the shift in the conversion curve towards progressively lower temperatures. The temperature at which 30% *o*-xylene conversion was reached (Fig. 3) first decreased, and then remained approximately constant for Cs_2O contents higher than 0.35 wt.%. Another peculiar aspect is that the samples having the highest Cs content showed a high catalytic activity at low temperature, while with increasing temperature the conversion levelled-off (this is particularly evident in Cs0.8 and in Cs1.0). This suggests a possible diffusional effect on the rate-determining step of the reaction for these samples, with a change from kinetic control to diffusional control, or alternatively from kinetic control with particle efficiency equal to 1.0 for the lower reaction temperatures, to an efficiency lower than 1.0 for the higher reaction temperatures. This also caused the trend reported in Fig. 3, relative to the temperature at which 70% conversion is reached: a minimum is clearly observed, obtained in correspondence with 0.35 wt.% Cs_2O.

Variations in the rate-determining step with increasing temperatures or diffusional contributions to the rate-determining step are known to occur for catalysts characterized by the presence of intrinsically very active sites, and usually lead to a considerable decrease in the apparent activation energy. This makes the reaction rate much less dependant on temperature than under conditions of full kinetic control. Thus, one possible hypothesis is that indeed the presence of increasing amounts of Cs caused an increase in the intrinsic vanadium activity, but that this finally led to a limited *o*-xylene conversion at relatively high temperatures due to the short diffusion path of the reactant in the pores.

The effect of Cs on selectivity to PA also was relevant, as shown in Fig. 3, which reports the selectivity at 70% *o*-xylene conversion as a function of Cs content in the samples. While for low Cs contents (i.e. in Cs0.1) no significant improvement in selectivity to PA was observed with respect to the undoped Cs0 sample, amounts of Cs higher than 0.1 wt.% Cs_2O led to a considerable increase in selectivity.

In order to check the presence of possible intraparticle diffusional effects on the rate-determining step, tests were carried out using catalyst particles with a lower characteristic length, i.e. ranging 250–420 μm in diameter instead of 250–590 μm. The results for the two different particle diameters (with the same amount of catalyst loaded in the reactor) are compared in Fig. 4 for sample Cs1.0; the *o*-xylene conversion and the selectivity to PA are plotted as functions of temperature. Decreasing the particle size led to an increase in activity, with a shift in the conversion curve towards lower temperatures, as a consequence of the

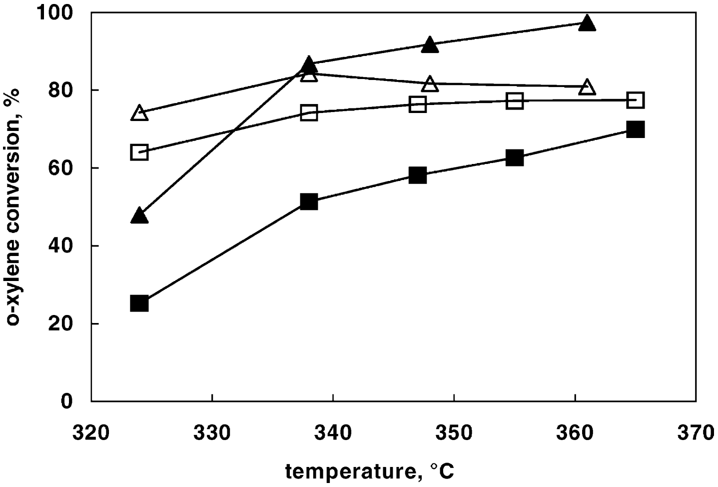

Fig. 4. Conversion of *o*-xylene (filled symbols) and selectivity to PA (open symbols) as functions of temperature for the Cs1.0 catalyst, with particle size in the 250–420 μm (▲), and 250–590 μm (■) range. Conditions as in Fig. 2.

higher availability of active sites as compared with a less-than-1 particle efficiency. Moreover, the conversion was now more dependent on temperature, at least up to 340 °C, at which 85% *o*-xylene conversion was reached (however, a contribution of diffusion still cannot be excluded for temperatures higher than 340 °C). A slight improvement in selectivity to PA was also observed.

Fig. 5 plots the selectivity to PA and the sum of selectivities to *o*-tolualdehyde, *o*-toluic acid, phthalide and PA as functions of the *o*-xylene conversion, for the Cs0 and Cs0.35 samples. With reference to the reaction scheme illustrated in Fig. 6 [1,2,14], the sum of the selectivities to *o*-tolualdehyde, *o*-toluic acid, phthalide and PA represents the ability of the catalyst to catalyze the selective, multi-step pathway leading to

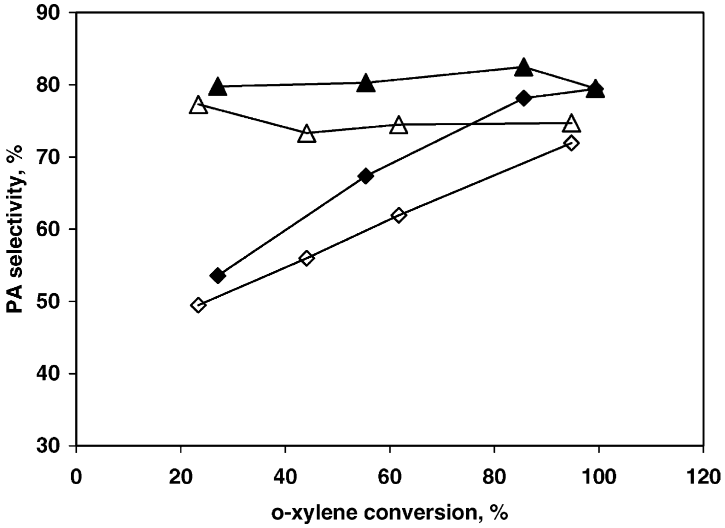

Fig. 5. Selectivity to PA (◆) and to *o*-tolualdehyde + *o*-toluic acid + phthalide + PA (▲) as a function of the *o*-xylene conversion for the Cs0 (open symbols) and Cs0.35 (filled symbols) catalysts. Conditions as in Fig. 2.

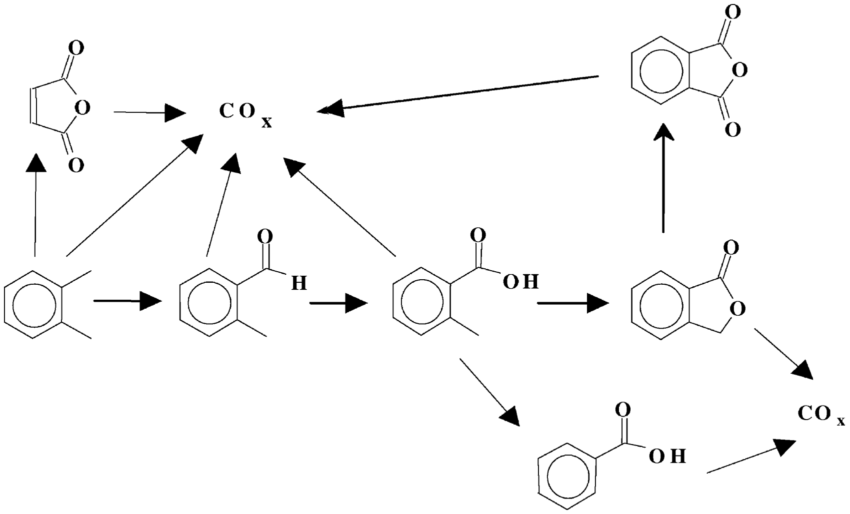

Fig. 6. Reaction scheme for the oxidation of *o*-xylene with V/Ti/O catalysts.

PA rather than the non-selective pathways leading to products of degradation/combustion: carbon oxides; maleic anhydride; benzoic acid. The data reported in Fig. 5 indicate that the selectivity to PA was similar for the two catalysts at low *o*-xylene conversion, but for higher conversions it became ≈10 points percent higher in the Cs0.35 sample than in the Cs0 sample. The same difference between the two samples is observed if we compare the sum of the selectivities to the products belonging to the reaction pathway leading to PA. This indicates that the better selectivity in the Cs-containing samples mainly derives from the higher overall rate of the selective reaction pathway leading to PA as compared to the rates of unselective oxidative degradation over the reaction intermediates.

Catalytic tests were carried out with different concentrations of *o*-xylene in the feed, while keeping constant the oxygen partial pressure (always present in large excess), at 355 °C for Cs0 and at 335 °C for Cs0.35 (Fig. 7). Conditions and catalysts were chosen so as to avoid the range of particle efficiency less-than-1. Substantial differences are observed between the two samples:

(1) The conversion rapidly decreased with increasing *o*-xylene concentration in the feed in the case of the Cs0.35 catalyst, which corresponded to an overall productivity (moles of *o*-xylene converted per unit time and unit catalyst weight, also plotted in Fig. 7) which was substantially independent of the hydrocarbon concentration. Different was the case for the Cs0 catalyst, for which the conversion only slightly declined on increasing the *o*-xylene concentration, yielding an overall productivity which increased as the latter parameter increased, up to a saturation effect which was met at around 1.5 mol% *o*-xylene in the feed. The different behaviors of the Cs0 and Cs0.35 catalysts with respect to variations in *o*-xylene partial pressures suggests that the rate of vanadium reduction by *o*-xylene is greatly affected by Cs addition.

(2) The selectivity to PA was considerably higher for the Cs0.35 sample than for the Cs0 sample for low *o*-xylene concentrations in the feed, but the situation reversed above 1.5% *o*-xylene in the feed, the undoped Cs0 catalyst becoming slightly more selective than the doped one. In fact, while with the Cs0 sample the selectivity to PA was approximately independent of the *o*-xylene concentration, it did decrease with increasing *o*-xylene concentration with the Cs0.35 sample. The decrease in selectivity occurred with an increase in the formation of reaction intermediates, *o*-tolualdehyde (mainly), phthalide and *o*-toluic acid, as a consequence of the different conversions achieved,

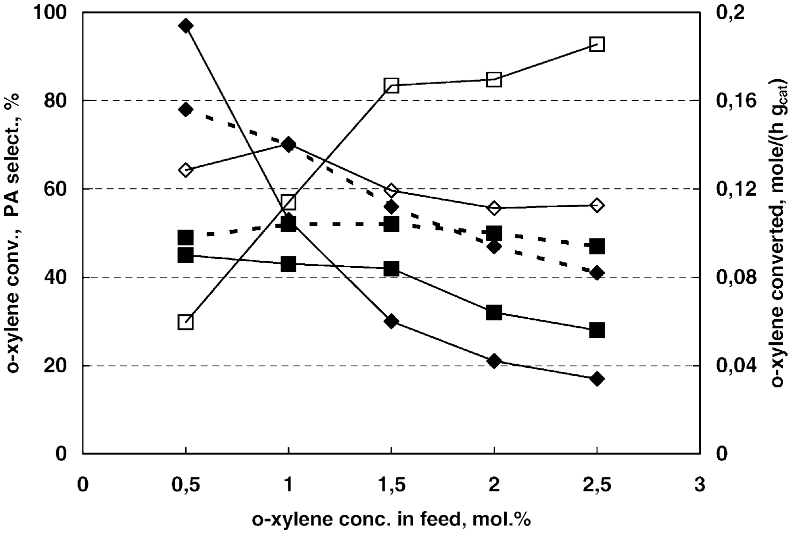

Fig. 7. Effect of *o*-xylene concentration in the feed on *o*-xylene conversion (filled symbols, solid lines), on the overall productivity (open symbols, full lines) and on the selectivity to PA (filled symbols, dotted lines) on Cs0 (■) (T, 355 °C) and Cs0.35 (◆) (T, 335 °C), residence time 0.3 s.

while the selectivity to carbon oxides was only slightly affected by this parameter.

Further tests were made using different oxygen concentrations in the feed, while keeping the *o*-xylene concentration in the feed constant (1 mol%); the other experimental conditions and the catalysts were the same as those of Fig. 7. Results are plotted in Fig. 8: for both samples the conversion of *o*-xylene increased with increasing oxygen concentration in the feed, but

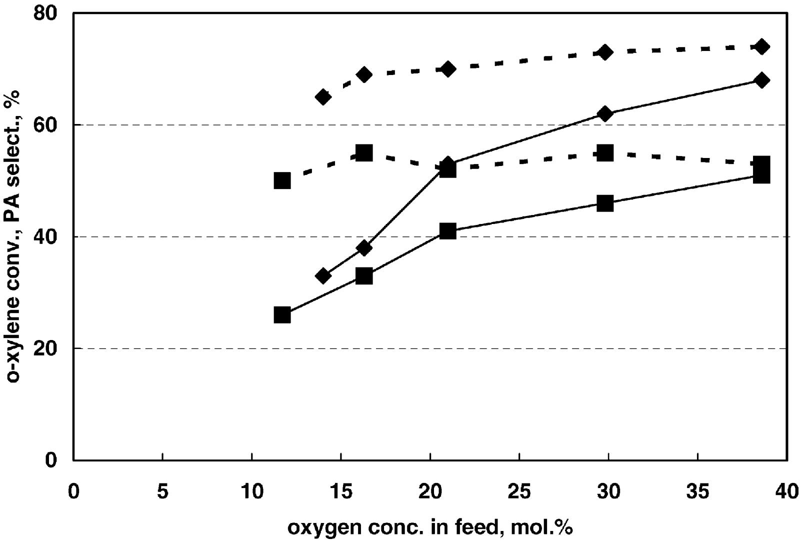

Fig. 8. Effect of oxygen concentration in the feed on *o*-xylene conversion (solid lines), and on the selectivity to PA (dotted lines) on samples Cs0 (■) and Cs0.35 (◆). Conditions as in Fig. 7.

for the Cs0.35 sample the conversion clearly showed a stronger dependence on this parameter than the Cs0 sample. Therefore in the former catalyst the conversion of *o*-xylene was not affected by the hydrocarbon concentration, while it was affected by the oxygen concentration. Different was the case for the Cs0 catalyst, for which the conversion was a function of the partial pressure of both reactants.

The selectivity to PA also showed a different trend with the two catalysts (Fig. 8). Whereas in the Cs0 sample the selectivity was unaffected by oxygen concentration, in the Cs0.35 sample the selectivity slightly increased with increasing this parameter. This occurred mainly at the expense of *o*-tolualdehyde, the selectivity of which showed a corresponding decrease, while the formation of carbon oxides remained practically unchanged. This means that an increase in oxygen partial pressure accelerates the rate of the selective pathway leading to PA more than the undesired parallel routes to the degradation products. In the Cs0 sample, the effect of oxygen on selectivity to *o*-tolualdehyde was similar (a progressive decrease with increasing oxygen concentration), but in this case the intermediate was mainly converted to carbon oxides (the selectivity of which increased) rather than to PA.

Results obtained indicate that the nature of the active sites drastically changes in the presence of Cs, with a variation of the redox properties of V sites: this point was further investigated by means of TPR/TPO measurements.

3.2. TPR tests

The TPR tests were carried out in order to determine the effect of Cs on the redox properties of the vanadium species. A reference sample was prepared by mechanical mixing and calcination of TiO_2 and V_2O_5 (in the same relative amounts and using the same titania as for the impregnated samples) in order to better assign the experimental reduction peaks. Fig. 9 compares the TPR and TPO (the latter on the pre-reduced catalysts) profiles of the reference sample and of the Cs0 sample.

In the reference sample there is a strong reduction peak with a maximum at 620 °C, due to the reduction of crystalline V_2O_5, and a shoulder at lower temperatures (around 530 °C) which can be related to some vanadia species which spread over titania during the mixing of the two oxides and calcination. The same two peaks falling at the same temperatures are observed for the Cs0 sample, but with different relative intensity, as expected on the basis of the relative amounts of the two different vanadia species in the samples (i.e. crystalline vanadia and spread vanadia). This confirms literature indications about the lower reducibility of vanadium present in the crystalline form as compared to that of the vanadium species spread on the support and chemically interacting with it [11,12,15,16].

TPR tests were carried out for all Cs*x* samples. In all cases a main reduction peak was present with a maximum at temperatures between 530 and 570 °C, which however progressively shifted towards higher temperatures with increasing Cs content in the samples, and a second reduction peak of minor intensity at higher temperatures, around 620 °C. Only for Cs0.8 and Cs1.0 was an additional peak at 500 and 530 °C, respectively, observed, which may be related to the intermetallic Cs/V/O compound detected by XRD (see Fig. 1). The shift in the most intense reduction peak (assigned to V species spread on the support) towards higher temperatures indicates a decrease in vanadium reducibility.

Since data shown in Fig. 7 suggest that the rate of vanadium reduction by *o*-xylene is increased as a consequence of Cs addition (the rate of reaction becomes independent on *o*-xylene concentration), no relationship between V reducibility and catalytic activity for increasing Cs contents can be deduced on the basis of the TPR tests. Neither is it possible to attribute the increased activity of Cs-containing samples to the V species which is reduced at the lowest temperature in the Cs0.8 and Cs1.0 samples, since the improvement in catalytic activity was already observed with the samples having the lowest Cs contents (Cs0.1 and Cs0.35).

One possible interpretation for the observed phenomena is that the Cs0.35 catalyst possesses intrinsically more reactive sites, but that the overall number of sites is lower than for the Cs0 sample, and the surface becomes saturated even for low *o*-xylene concentrations in the feed. Therefore, the Cs0.35 sample is more active than the Cs0, but the overall rate of *o*-xylene transformation becomes independent of the hydrocarbon concentration already for very

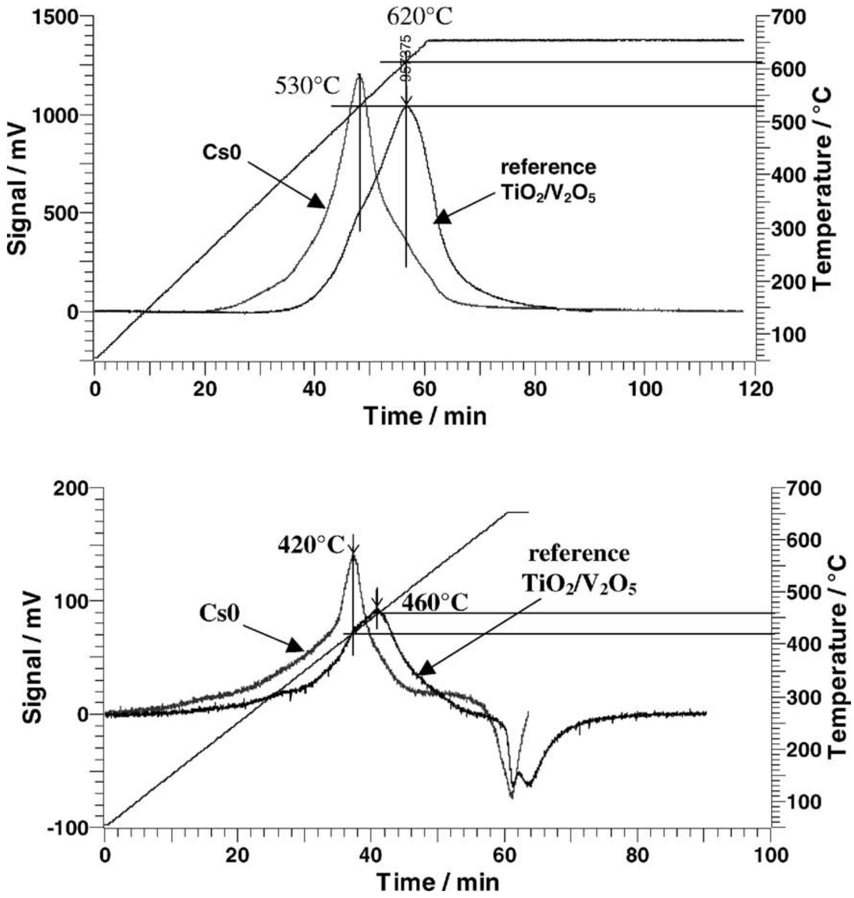

Fig. 9. TPR (top) and TPO on pre-reduced catalyst (bottom) profiles of Cs0 and of the reference sample prepared by mixing and calcination of TiO_2 and V_2O_5.

low values of it (Fig. 7). The same effect occurs only for higher hydrocarbon concentrations in the case of the Cs0 sample. Under the hypothesis of a redox-type mechanism, this also means that in the case of the Cs0.35 catalyst the step of catalyst reduction by the hydrocarbon is not the rate-limiting step: in fact, the rate is not affected by the partial pressure of *o*-xylene (Fig. 7). Analogously, the active sites in Cs0.35 are intrinsically more selective to PA than sites in Cs0; however, this effect is made nil when the concentration of *o*-xylene is progressively increased, due to the saturation of the surface and to the lower availability of O-insertion sites. One possible way to overcome this saturation effect is to increase the oxygen partial pressure, as shown by results reported in Fig. 8.

3.3. TPO tests

In the re-oxidation profile of the Cs0 sample which had been pre-reduced during TPR (Fig. 9, bottom), a main peak was observed with a maximum at 420 °C, accompanied by a shoulder at lower temperatures. The TPO profile of the reference sample (prepared by mixing and calcination of titania and vanadia) showed a main peak at 460 °C with a shoulder at 420 °C. It is thus possible to assign the latter peak to the re-oxidation of vanadium species spread on titania, the highest temperature peak (at 460 °C) instead can be assigned to the re-oxidation of pre-reduced crystalline vanadia. With increasing cesium content in the Cs*x* samples (Fig. 10), the main re-oxidation peak was splitted into two peaks (i) a major peak the maximum

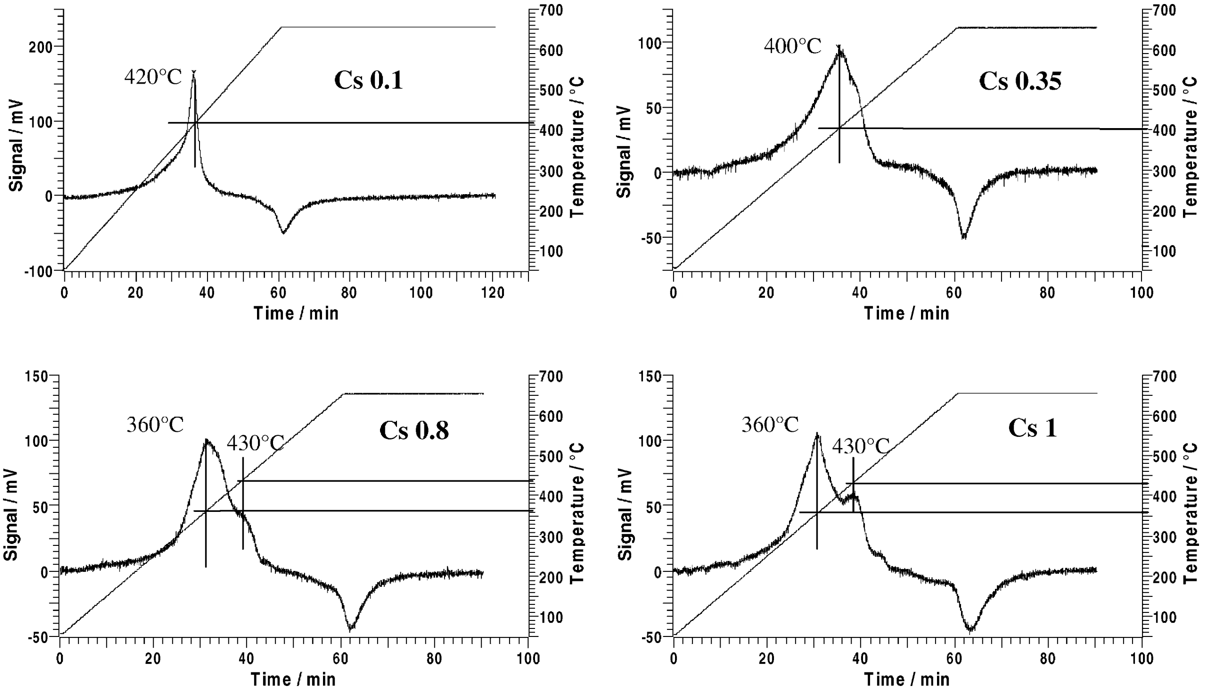

Fig. 10. TPO profiles of pre-reduced catalysts at increasing Cs contents.

of which progressively shifted from 420 °C (for Cs0 and Cs0.1) towards lower temperatures, becoming positioned at 360 °C for Cs0.8 and Cs1.0, and (ii) a less intense one at ≈430 °C. The split is well-evident in the samples having the highest Cs content. A possible assignment of the less intense peak is to the re-oxidation of the vanadium species in the intermetallic crystalline compound $Cs_2V_6O_{16}$.

In TPO profiles of all samples a negative peak was also observed, occurring at 630–650 °C, which can be attributed to the release of oxygen from vanadium oxide, with development of the reduced Magneli phases. The peak is negative due to the fact that the thermo-conductivity detector of the instrument compares the oxygen concentration fed to the catalyst with that exiting the catalytic bed: generation of oxygen, instead of its consumption, causes the development of a negative peak. This attribution was confirmed by carrying out a temperature programmed treatment of the Cs0 sample in a nitrogen flow (Fig. 11, top). A peak falling at the same temperature as the negative one observed in Fig. 10 developed, but of positive intensity, due to the heat-conductive properties of molecular oxygen as compared to the reference molecular nitrogen. The release of oxygen from the catalyst changed the properties of the latter, as demonstrated by repeating once again the TPR measurement immediately after the TPO measurement (Fig. 11, middle). The peak corresponding to the vanadium reduction was now less intense than that obtained in the first TPR measurement (also reported for comparison), in agreement with a lower oxygen content for the catalyst after the TPO test. Besides being less intense, the shape of the reduction peak during the second TPR measurement was considerably different from that which developed with the first TPR measurement.

When instead the TPR measurement was repeated after the TPO test, but interrupting the latter measurement before the appearance of the negative peak associated to oxygen release, the resulting reduction profile was very similar to that of the first TPR measurement (Fig. 11, bottom). This also confirms that during the first TPR measurement no irreversible structural or morphological changes occurred in the catalyst (e.g. transformation of anatase into rutile with formation of solid solutions of V in rutile), or that at

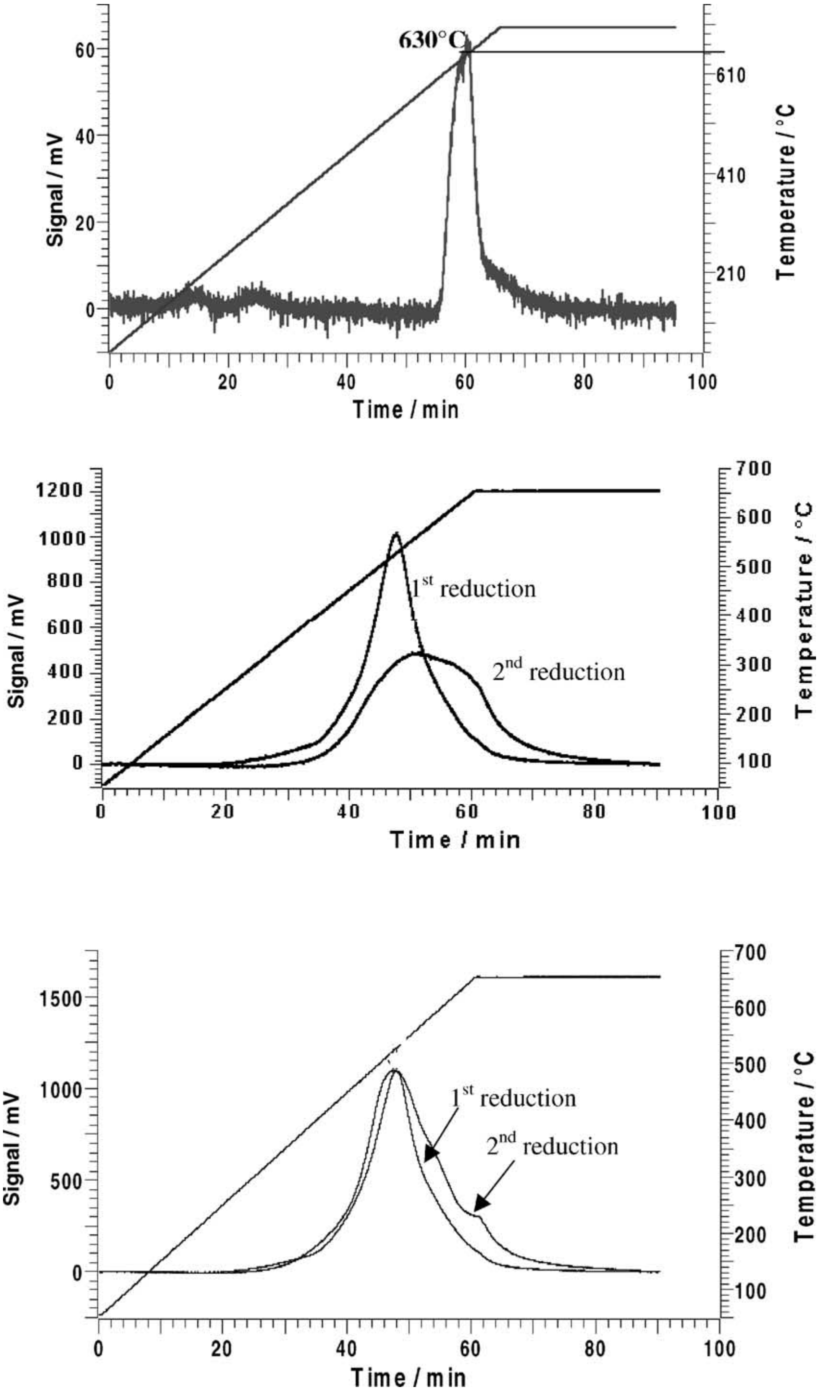

Fig. 11. Thermal-programmed profile in a nitrogen flow of calcined Cs0 (top) and TPR profile of calcined Cs0 (first reduction), TPR profile of the same sample after it had been subjected to the TPO measurement up to 650 °C (second reduction) (middle), TPR profile of calcined Cs0 (first reduction), and TPR profile of the same sample after it had been subjected to the TPO measurement up to 450 °C (second reduction) (bottom).

least any change occurring was not so extensive as to dramatically affect the vanadium redox properties, provided the temperature gradient during TPO was stopped before the spontaneous release of oxygen. This also confirms the validity of the measurements adopted, and the possibility to use the technique for developing reliable comparisons between catalysts.

TPO tests on pre-reduced Cs*x* catalysts (Fig. 10) evidenced that the re-oxidizability of V increased when the Cs content in the catalysts increased. This also corresponds to the experimental evidence that in Cs-doped samples the conversion was not affected by *o*-xylene partial pressure, while it was affected by oxygen partial pressure, suggesting an important role of vanadium re-oxidation in the rate-determining step. Thus, it seems that a possible relationship exists between the catalyst re-oxidizability and the increase in catalytic activity occurring as a consequence of Cs addition in the V/Ti/O catalyst. This relationship is summarized in Fig. 12, which reports (i) the temperature at which 30% *o*-xylene conversion was reached, (ii) the temperature at which the most intense reduction peak in TPR tests occurred and (iii) the temperature at which the most intense re-oxidation peaks occurred, as functions of the Cs content in the samples.

Cesium affected the catalyst activity even for very low amounts of it (in the Cs0.1 sample the V/Cs atomic ratio was equal to 108). This indicates that the interaction between Cs and the active phase should be interpreted more in terms of a modification of collective properties rather than a change in localized or short-range properties. In the case of potassium, Deo and Wachs [8] have proposed that the dopant may affect the strength of V=O bonds, as a consequence of the coordination to terminal O or to O ions bridging vanadium to the support. This implies a localized effect, which however does not explain why in our samples even for very low Cs contents a considerable effect on catalytic performance was observed. When the amount of Cs approached that of vanadium (i.e. for V/Cs atomic ratios lower than 15–20), an additional effect was the development of the mixed compound of stoichiometry $Cs_2V_6O_{16}$, which also showed redox properties that are different from those of crystalline vanadia or of vanadia spread on the support. This may also contribute to affect the catalytic properties of samples having the highest Cs contents, but our data seem to suggest that the redox properties of vanadia species spread on the support (which are known to constitute the active sites for the reaction) may be considerably affected even for very low amounts of the dopant.

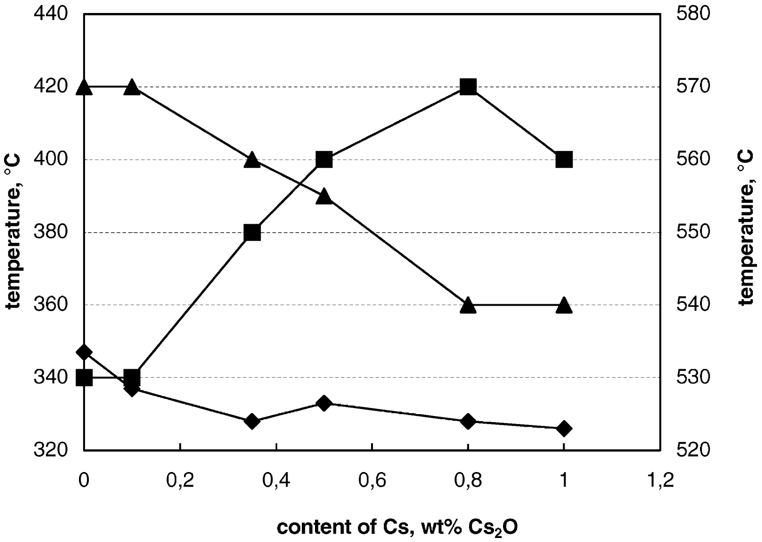

Fig. 12. Temperature for 30% conversion (◆, left scale), temperature of the main peak of reduction in TPR measurements (■, right scale), and temperature of the main peak of re-oxidation in TPO measurements of the pre-reduced samples (▲, left scale), as functions of the Cs content in the catalysts.

4. Conclusions

The effect of Cs on chemical–physical features and catalytic performance of V/Ti/O, catalyst for the selective oxidation of *o*-xylene to PA, was studied. Cesium was found to belong to the class of "interacting additives" [8], and the interaction between vanadium and cesium had important consequences on the activity and on the redox properties of V even when the concentration of the alkali metal ion on titania was two orders of magnitude less than that of vanadium. This implies a long-range effect which corresponds to an enhancement of the electron-donating power (i.e. Lewis basicity) of the entire active phase, rather than to the formation of a specific intermetallic compound or to a localized modification of V sites to which Cs is directly bound. Specifically, the addition of increasing amounts of Cs led to the development of an active phase which in its higher oxidation state was progressively less susceptible to reduction, but which in its lower oxidation state was more and more prone to be re-oxidized by molecular oxygen. The effect is thus analogous to that which is found in n-type semiconductors when a "basic" ion introduces additional electron–donor levels in the band gap, thus improving the reducing properties of the material. On the other hand, these levels make the reduction of the oxidized vanadium less easy, due to its lower electron-affinity (i.e. Lewis acidity).

The above described effects had profound implications on catalytic performance. Since the reaction rate was affected by the oxygen partial pressure in both Cs-doped and undoped catalysts, and since therefore the re-oxidation of reduced vanadium sites contributed to determine the rate of the reaction, the addition of Cs considerably improved the catalyst activity and thus the *o*-xylene conversion achieved for defined reaction conditions. On the other hand, Cs addition made the number of sites available for electron exchange with *o*-xylene lower than in the undoped Cs0 catalyst, which, in turn, implied that even for relatively low *o*-xylene concentrations in the feed the active phase became saturated with the hydrocarbon. Under these conditions, the reaction became independent of the hydrocarbon concentration, while it was greatly affected by the oxygen concentration. For low concentrations of *o*-xylene in feed (e.g. less than 1% *o*-xylene) a considerable increase in selectivity to PA was observed in the Cs-doped samples with respect to the Cs0 sample.

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