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Anatase-supported vanadium oxide catalysts for *o*-xylene oxidation: From consolidated certainties to unexpected effects

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ABSTRACT

In this paper some aspects of the reaction of *o*-xylene oxidation, catalysed by anatase-supported vanadium oxide, are re-examined and compared with the scientific and patent literature. Specifically, the effect of vanadia loading on turnover frequency and on the distribution of products has been investigated, using catalysts having sub-monolayer and above-monolayer vanadium oxide deposited on a high-purity anatase support. It was found that even catalysts having less-than-monolayer vanadia loading, containing isolated or oligomeric VO_4 species, may give good selectivity to phthalic anhydride, provided the support does not catalyze the formation of heavy compounds. Moreover, the effect of water on the reactivity and chemical–physical characteristics of catalysts was studied by means of *in situ* Raman spectroscopy. Steam promoted dynamic reversible phenomena occurring at the catalyst surface, by facilitating the dispersion of bulk vanadium oxide and therefore increasing the catalyst activity.

1. Introduction

Vanadium oxide-based catalysts are used in the synthesis of important chemicals, either in the form of supported metal oxide, e.g., in the manufacture of phthalic anhydride by *o*-xylene oxidation, of sulphuric acid by oxidation of SO_2 and in the reduction of NO_x with ammonia, or in the form of multicomponent mixed oxides and oxysalts, e.g., in the oxidation of *n*-butane (V/P/O) and of benzene (supported V/Mo/O) to maleic anhydride [1–6].

In literature, several papers discuss the chemical–physical features and catalytic properties of titania-supported vanadium oxide-based catalysts (V/Ti/O) in oxidation catalysis [7–18]. However, little attention has been given to one aspect that may have profound implications on the catalytic performance, i.e., the role of gas-phase components. In fact, in the industrial practice, the vanadium oxide-based catalysts need the addition of gas-phase promoters in the feed stream, that although do not have a direct role in the reaction stoichiometry, when present give a considerable improvement of catalytic performance.

In the present paper, we investigate the dynamic phenomena occurring at the V/Ti/O surface, catalyst for *o*-xylene oxidation to phthalic anhydride, in the presence of steam, a component of the reaction environment in the oxidation reactions, and also examine the role of vanadium oxide loading on V/Ti/O reactivity.

2. Experimental

Catalysts were prepared with the wet impregnation technique: an aqueous solution containing the desired amount of NH_4VO_3 was added to the TiO_2 support (anatase, having a specific surface area of 22.5 m^2/g). In order to avoid problems deriving from the low solubility of NH_4VO_3, that might lead to the deposition of salt agglomerates and to the formation of bulk vanadia in final catalysts, we used a concentration of the salt in water (50 °C) that was approximately 1/10th of the solubility limit of NH_4VO_3 (0.4 in 100 mL water, the solubility limit being 4.8 g in 100 mL water, at 20 °C). 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.

Titania was a high-purity commercial anatase sample, containing the following impurities: Na 25–30 wt ppm, K 20–25 wt ppm, Fe 25–30 wt ppm, P_2O_5 0.07 wt%. These quantities are by far lower than those supposed to affect the reactivity properties of titania in V/Ti/O catalysts ([7] and references therein). However, small quantities of alkali metal ions can be useful to neutralize surface Ti–OH groups, that may catalyze the formation of heavy compounds [7]. No rutile impurity was detected by means of X-ray diffraction and Raman spectroscopy in our TiO_2 sample.

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The catalysts were characterized by means of X-ray diffraction and Raman spectroscopy. The XRD diffraction patterns were taken using a Philips *PW 1710* apparatus, with Cu Kα (λ = 1.5406 Å) as radiation source. Raman studies were performed using a Renishaw 1000 instrument, equipped with a Leica DMLM microscope, and laser source Argon ion (514 nm). *In situ* measurements were performed in a Linkam TS1500 heated cell, by feeding vapours of wet air, containing either 1 or 3 vol.% water; the concentration of steam was varied by bubbling the dry air stream in a water-containing vessel, maintained at controlled temperature.

Catalytic tests were carried out in a laboratory continuous-flow, fixed-bed reactor at atmospheric pressure. The size of catalyst particles ranged from 250 to 590 μm. The feed composition was either 1 mol% *o*-xylene in air, or 1 mol% *o*-xylene and 3 mol% steam in air. The products in the outlet stream were condensed in HPLC-grade acetone. The reactants and the products were analysed 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.

3. Results and discussion

3.1. The effect of the vanadia loading revisited

The main component of the industrial catalyst for *o*-xylene oxidation to phthalic anhydride is vanadium oxide, dispersed over TiO_2 anatase support. However, an important role is also played by dopants, e.g., alkali metal ions oxides (K_2O and Cs_2O), P_2O_5, and oxides of transition or post-transition elements, such as Mo and Sb.

The amount of vanadium oxide loading is one important parameter [7–18]; in the industrial practice, the amount of active component is usually comprised between 5 and 10 wt% V_2O_5, for titania surface area comprised between 15 and 30 m^2/g. This vanadium oxide loading is close to or higher than that one corresponding to the monolayer coverage of the support. This is necessary in order to minimize the reactivity contribution of the bare support that can be detrimental for the selectivity to phthalic anhydride. Furthermore, it is believed that a high surface density of vanadium ions sites is necessary for this complex reaction, which requires the transfer of several O^{2-} species from the solid to the alkylaromatic.

The effect of increasing loading of vanadium oxide on the nature of the V species, with a TiO_2 of 22.5 m^2/g, is illustrated in Fig. 1, showing the Raman spectra recorded at 360 °C, i.e., under conditions at which the VO_x species are dehydrated. It is shown that for a V_2O_5 content of 1 and 2 wt%, the predominant band was that at approximately 1030 cm^{-1}, assigned to the symmetric stretch of mono-oxo terminal V═O bond [19–23]. This band shifts slightly of a few cm^{-1}, e.g., from 1028 to 1032 cm^{-1}, with increased vanadia loading [23]. In our samples, the band fell at 1029 ± 1 cm^{-1}, and apparently there was no shift of the band for increasing vanadium loading; therefore the attribution either to monomeric isolated VO_4 species or to oligomeric species is uncertain. The 1 wt% V_2O_5 corresponds to approximate the 40% of the theoretical monolayer, that would indicate the preferred formation of oligomeric species; however, in previous works, evidences were obtained that in this sample the monomeric, isolated species was the prevailing one [24].

The broad band between 900 and 950 cm^{-1} is attributable to the internal vibration of the V–O–V bond in oligomeric vanadium species [19,20]. However, this attribution was recently confuted in the case of alumina-supported vanadium oxide, being the band in this region due to interface mode, i.e., V–O–Al bond [25].

The band at 997 cm^{-1} is typical of bulk vanadium oxide; it was observed already in the sample containing the 2 wt% V_2O_5, and its intensity grew remarkably when the vanadia loading was increased above the monolayer. The monolayer is defined as the highest vanadia loading that produces only surface VO_4 species and not spectrally distinct V_2O_5 microcrystallites, as measured by Raman spectroscopy [2]. Experimental determinations agree that for the TiO_2 support, the monolayer corresponds to approximately 7.9 V atoms per nm^2, that is about 0.11 wt% V_2O_5 per square meter of titania [20–23]. However, the maximum vanadium oxide loading dispersed on anatase, without the formation of bulk vanadium oxide, may be a function of the preparation procedure adopted, ranging from 4 to 10 V atoms per nm^2 [3,7].

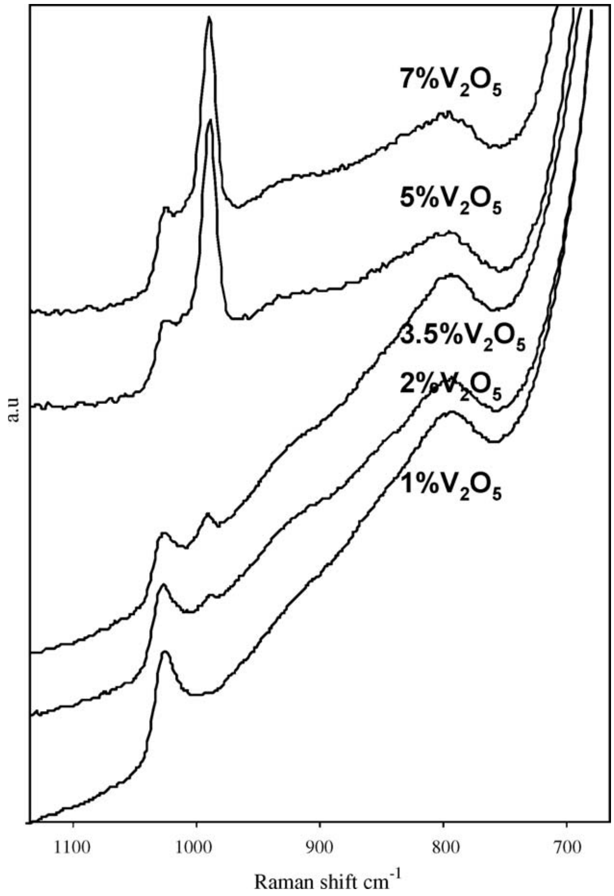

Fig. 1. Raman spectra of dehydrated V/Ti/O catalysts having increasing amounts of V_2O_5 loading.

Fig. 2a plots the rate of *o*-xylene transformation per mol of V (TOF) at 334 °C as a function of the vanadia loading; the figure also compiles the temperature at which 60% *o*-xylene conversion was obtained. It is shown that the TOF decreased when the vanadia loading was increased; the most relevant decrease of activity was observed for the sample containing the 3.5 wt% V_2O_5, in which the formation of bulk vanadia was evident (see Raman spectra in Fig. 1).

A decrease of the activity for vanadia contents above the monolayer is an expected effect, because bulk vanadia is less active than polyvanadate due to the exposure of fewer sites per unit weight of active phase. Furthermore, the vanadia crystallites are sitting on top of the surface vanadium oxide monolayer and further decrease the number of exposed surface vanadia sites. Due to these reasons, the experimental TOF indeed is an apparent value when measured for samples having supra-monolayer vanadium oxide loading. In contrast with these data, however, some authors reported that above the monolayer coverage the activity and

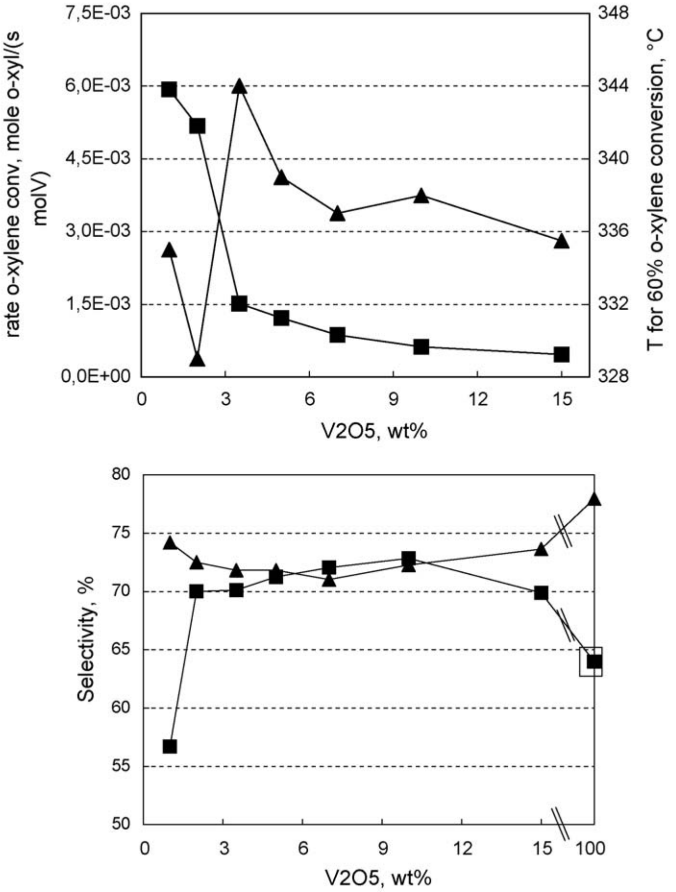

Fig. 2. Top: integral rate of *o*-xylene conversion at 334 °C per unit mole of V (■) and temperature for 60% *o*-xylene conversion (▲) as functions of the overall vanadia loading in V/Ti/O catalysts. Bottom: selectivity to *o*-tolualdehyde + *o*-toluic acid + phthalaldehyde + phthalide + phthalic anhydride + phthalic acid at 40–55% *o*-xylene conversion (▲) and selectivity to phthalic anhydride + phthalic acid at 98% *o*-xylene conversion (■) as functions of the overall vanadia loading in V/Ti/O catalysts.

selectivity were essentially not influenced by the vanadia content [26], but the formation of crystalline V_2O_5 led to a decrease of activity.

In the case of *o*-xylene oxidation with sub-monolayer V/Ti/O catalysts, in general higher vanadium oxide loading lead to an increase of conversion [26,27], but a comparison of the V-specific activity was not reported. It is worth reminding that the presence of bare titania surface may lead to the deposition of heavy compounds on the catalyst surface, responsible for missing C in the C balance, that poison the isolated V species and lead to quick catalyst deactivation [8]; the characteristics of the titania support may greatly affect these deactivation phenomena. With our sub-monolayer samples, the C balance was around 96–98%, when the by-products phthalic acid and phthalaldehyde (products that have never been taken into consideration before in the literature) were also included [28]. Therefore, deactivation with our less-than-monolayer 1 and 2 wt% V_2O_5 catalysts was negligible; this made possible to evaluate the catalytic activity in the absence of phenomena that might affect it.

The plot of Fig. 2a indicates that the most reactive species is the dispersed VO_4. The decrease of activity shown in the sub-monolayer region may be attributed either to a lower activity of the V–O bond involved in the rate-determining step of the reaction, or to a lower accessibility of the active sites due to the development of polymeric species. A possible involvement of the V–O–Ti bond in *o*-xylene activation, as proposed for methanol oxidation catalysed by monolayer vanadium oxide [29], may also fit with the experimental trend; in fact, the number of V–O–Ti bonds per V atom decreases with an increase of the degree of condensation of VO_4 units.

The effect of the vanadium oxide loading on selectivity is shown in Fig. 2b, that compiles the overall selectivity to *o*-tolualdehyde + *o*-toluic acid + phthalide + phthalaldehyde + phthalic anhydride + phthalic acid (that is, the overall selectivity to C_8 oxygenates, including reaction intermediates precursors of phthalic anhydride formation) at 40–55% *o*-xylene conversion and at 98% *o*-xylene conversion; under the latter conditions, the selectivity to the intermediates was close to zero. The trend at moderate conversion is different from that one previously reported in the literature [27], especially if the sub-monolayer catalysts are taken into consideration; this discrepancy may be attributed to a different role of the bare titania support, whose characteristics may greatly affect the performance.

The 1 wt% V_2O_5 catalyst gave the best overall selectivity at moderate *o*-xylene conversion, but showed the lowest selectivity to phthalic anhydride + phthalic acid at high hydrocarbon conversion. The increase of the vanadia content led to a small but non-negligible decrease of the selectivity at moderate conversion, the minimum being observed with the catalyst having the 5 wt% V_2O_5. The selectivity at high conversion, on the contrary, was the highest with catalysts having the 7 and the 10 wt% V_2O_5.

These data clearly indicate that the best performance is shown by catalysts having more than the monolayer coverage, that corresponds to the vanadium oxide content claimed in the patent literature [30–34], and agrees with most of the scientific literature reports. Apparently, this is necessary in order to limit undesired consecutive reactions occurring on phthalic anhydride, such as combustion or hydrolysis to yield phthalic acid, that at high temperature may be the precursor for the formation of carbon oxides.

Interestingly, Fig. 2b also shows that with catalysts having 5–10 wt% V_2O_5 the selectivity at high *o*-xylene conversion was similar to the overall selectivity to C_8 compounds obtained at medium conversion. This suggests that with these catalysts there is no important contribution of consecutive reactions limiting the selectivity to phthalic anhydride. On the other hand, with catalysts having less than 5 wt% and more than 10 wt% V_2O_5, the selectivity at high conversion was lower than that obtained at medium *o*-xylene conversion. This confirms the role of crystalline V_2O_5 and of anatase in promoting the high-temperature consecutive reactions on phthalic anhydride [1,2,8]. It is worth noting that the unsupported bulk V_2O_5 gave 44% conversion at 388 °C, with an overall selectivity to phthalic anhydride + intermediates of 79%, and of 64% at 98% conversion (413 °C) (Fig. 2b). Although much less active than titania-supported vanadium oxide [35], the selectivity shown by the bulk V_2O_5 at moderate conversion was even better than that one of the more-than-monolayer catalyst.

On the other hand, data in Fig. 2b also may explain why more recent patents claim the use of catalysts loaded with lower vanadia content (e.g., less than 5 wt% V_2O_5) for the first layer of the multi-layer reactor employed in the industrial operation [32,33]. This catalyst in fact gives the lowest selectivity to undesired by-products (benzoic acid, maleic anhydride and carbon oxides) in the medium conversion interval, that is that one occurring in the first catalytic layers. By the way, the less-than-monolayer catalyst also was remarkably active (Fig. 2a).

The performance of the 1 wt% V_2O_5 also indicates that a high surface density of VO_x species is not a requisite for the selective transformation of *o*-xylene to phthalic anhydride, in contrast with the general belief [7]. These data suggest that when the reaction network includes kinetically consecutive steps, and each reaction intermediate has to desorb into the gas phase before being re-adsorbed on another oxidized V sites and over there be transformed to the successive compound, almost isolated vanadium or oligomerized VO_4 units can perform this multi-step reaction, provided (a) the catalytically active surface is not saturated by reactants and intermediates, and (b) the rate-determining step in the redox process is the reduction of V sites by the hydrocarbon. This makes the majority of active sites be present in the oxidized form and hence be available for the interaction with *o*-xylene or with the intermediates. In this context, dopants also may play an important role [24,36,37].

3.2. The dynamic behaviour of V/Ti/O catalysts: the effect of steam

Fig. 3 shows the effect on catalytic performance of the 7 wt% V_2O_5 catalyst at 360 °C and residence time 0.13 s, when the reactor inlet is enriched with 3% steam; this corresponds to approximately twice the amount of water generated by the reaction itself at these reaction conditions.

It is shown that a progressive modification of the catalytic performance occurred within a few hours. After an initial rapid variation, the trend experimentally observed was that of an increase of *o*-xylene conversion; the latter finally reached a stable value after approximately 3–4 h of reaction with the steam-enriched feed. The increase of conversion also led to a better selectivity to phthalic anhydride, because of the lower selectivity to the reaction intermediates. Remarkably, the interruption of the steam addition in the feed led to the recovery of the initial performance within less than 2 h time-on-stream. This means that the effect of steam was reversible.

Different phenomena may be responsible for the effect experimentally observed: (a) a change of the catalyst surface temperature because of the different heat conduction properties of steam, as compared to the mixture of *o*-xylene, oxygen and nitrogen; however, in this case a decrease of the surface temperature and a decrease of the conversion would be the expected effects; (b) an effect of surface "cleaning", favouring the desorption of reaction intermediates and products and hence rendering the active sites more available for the activation of the alkylaromatic; it also may reduce carbon deposition; (c) a modification of the characteristics of the active sites; (d) an increase of the number of the active sites.

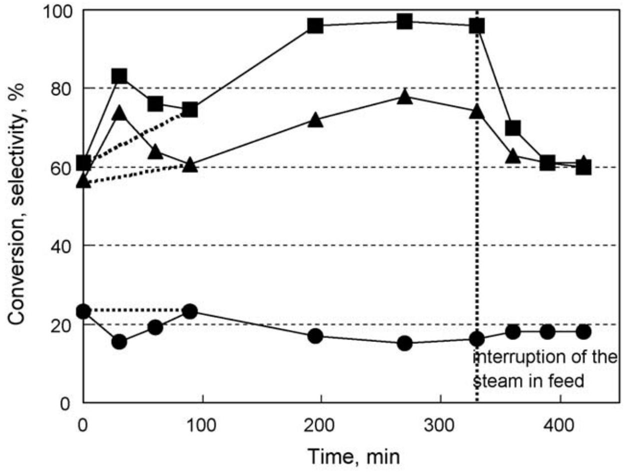

Fig. 3. *o*-Xylene conversion (■), selectivity to phthalic anhydride (▲) and to CO_x (●) at 360 °C as functions of time-on-stream after addition of 3 vol.% steam to the reactor inlet feed.

In literature, the effect of steam on the nature of V sites in supported vanadium oxide catalysts has been investigated by Wachs et al. [19,38]. It was found that moisture makes hydrogen bonding to the oxygen functionalities of the surface vanadia species; the H bonding was observed for the terminal V=O bond, the corresponding Raman band shifting to lower wavenumbers. Below 230 °C, water was also able to hydrolyse the V–O-support bond. However, at higher temperatures, no appreciable modification of the V surface species was found.

Fig. 4 shows the Raman spectra recorded *in situ* at 400 °C, by feeding a 3% steam in an air stream over the 7 wt% V_2O_5 catalyst. The spectra, recorded at increasing time of exposure to the wet stream, evidenced a progressive decrease of the intensity of the band at Raman shift 997 cm^{-1} associated to bulk vanadium oxide and of the other bands attributed to the latter compound as well, and an increase of intensity of the broad band falling between 900 and 1000 cm^{-1}. The band at 1029 cm^{-1} did not apparently undergo any modification. After this experiment, the temperature was lowered down to 360 °C, and dry air was fed to the catalyst; Fig. 5 compiles the Raman spectra recorded under the latter conditions. It is shown that after the interruption of the steam feed, the intensity of the band at 997 cm^{-1} increased; the spectrum originally recorded under a dry atmosphere was observed after 1 h the steam feed had been interrupted.

These results indicate that steam may favour the spreading of bulk vanadium oxide, with a corresponding increase of the number of active sites, and possibly also the formation of sites that are intrinsically more active than those in bulk vanadium oxide (Fig. 2a). The formation of smaller V_2O_5 nanoparticles, with an increased number of edge sites that give higher activity, also cannot be excluded.

It is well known that heating V_2O_5 at temperatures higher than the Tamman temperature (482 K) causes the spreading of the oxide over supports [39–41]. The driving force for this phenomenon is the lowering of the surface free energy by formation of the monolayer. However, high temperatures are required for surface diffusion or migration to occur at an appreciable rate. On the other hand, reaction-induced spreading of bulk metal oxides onto the surface of supports may occur during exothermal reactions, at temperatures lower than that required for thermal spreading [42]. Vanadia migration is favoured over well-developed anatase crystal planes [42]; at 450 °C spontaneous spreading takes place, controlled by diffusion of V species through the monolayer. It is worth noting that after reaction in our microreactor, the 5–10 wt% V_2O_5 (more-than-monolayer) catalysts, possessing bulk vanadia, still showed a Raman spectrum quite similar to that one before reaction. This means that the temperature that develops at the catalyst surface during the exothermal oxidation reaction is likely much higher than 400 °C, and that the latter conditions may thermodynamically favour segregation phenomena of vanadium oxide rather than its dispersion.

The effect of the steam added may be that one of lowering the catalyst surface temperature during reaction, that becomes closer to the temperature at which spreading phenomena may be both kinetically and thermodynamically favoured, i.e., approximately 400 °C. It is worth noting that when the reaction temperature in the Raman cell was raised up to 450 °C, the spreading phenomena that at 400 °C had occurred in a few hours did not occur at an appreciable extent within the same period of time. Moreover, when the same experiment of Fig. 4 was carried out with only ≈1% steam in air, or with no steam at all, no spreading of vanadium oxide was observed by *in situ* Raman measurements during 4 h on-stream. This means that the partial pressure of water is important in determining the kinetics of the transformation. This suggests that the main role of water was that of favouring the hydrolysis of

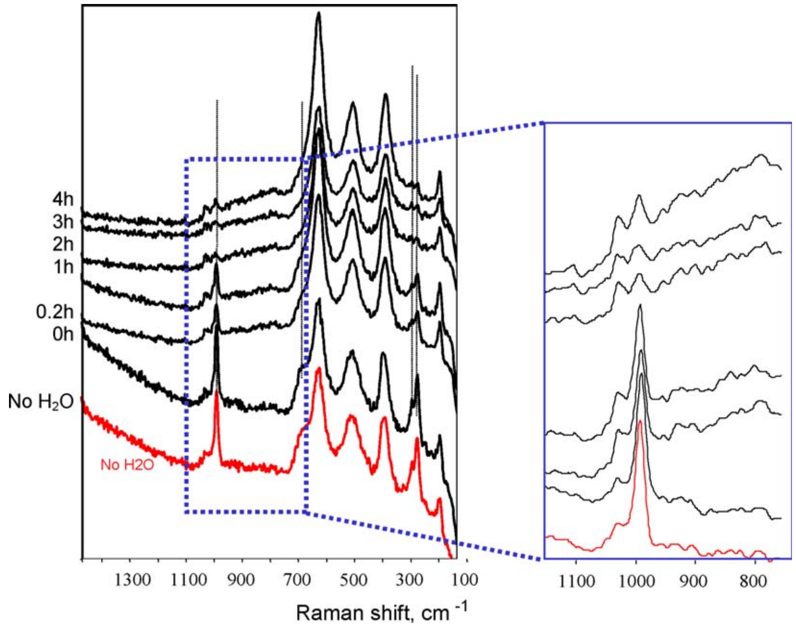

Fig. 4. Raman spectra recorded *in situ* at 400 °C in a 3 vol.% steam in air, at increasing times of exposure to the stream. Catalyst: 7 wt% V_2O_5–TiO_2.

V–O–V bonds in bulk vanadium oxide, with generation of mobile and reactive species. This caused an increase of the number of available active sites, and hence an enhancement of the catalytic activity.

The formation of stable V–O–Ti bonds (e.g., in polyvanadate) as a consequence of V spreading is unlikely, for two reasons: (a) due to the relatively high amount of vanadium oxide loading, most likely no titania surface was available for bonding with additional VO_x species; (b) the formation of a stable structure would not explain why the phenomenon was reversible (Figs. 3 and 5). In fact, when water was withdrawn from the feed, V species re-aggregated to yield back bulk vanadium oxide; in the reactor, this corresponded to a progressive lowering of the catalytic activity (Fig. 3).

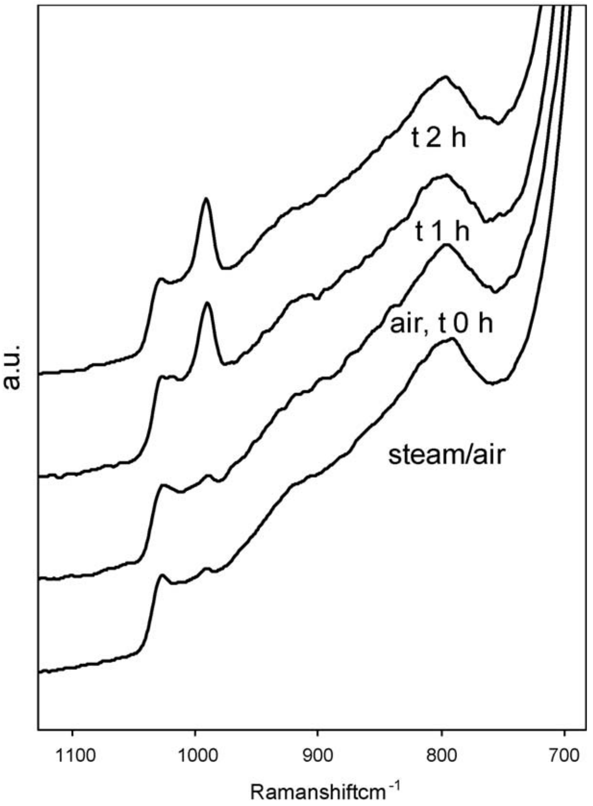

Fig. 5. Raman spectra recorded *in situ* at 360 °C, after changing the inlet stream from 3% steam-in-air to dry air. Catalyst: 7 wt% V_2O_5–TiO_2.

Noteworthy, the segregation of vanadium oxide after water withdrawal was experimentally observed during Raman *in situ* experiments only when the temperature in the cell was lowered down to 360 °C; in fact, at 400 °C, that is the temperature at which spreading phenomena had occurred in the presence of the wet stream, no formation of bulk vanadium oxide was observed within a few hours, during exposure of the catalyst to the dry air feed. This confirms that the two events, i.e., vanadium oxide dispersion and re-aggregation, only occur at well defined conditions, being the result of contrasting driving forces, function of the water partial pressure and of temperature. When the temperature is close to 400 °C, in fact, the hydrolysis of V–O–V bonds and the dispersion of V species, induced by the presence of steam, is kinetically favoured over the segregation into a bulk compound. On the other hand, at about 450 °C dehydration and segregation are favoured for thermodynamic reasons over hydrolysis and spreading, even in the presence of steam.

4. Conclusions

In this paper, we have re-examined the effect of the loading of vanadium oxide in V/Ti/O, catalysts for the selective oxidation of *o*-xylene to phthalic anhydride, in relation to the scientific and patent literature. In unpromoted V/Ti/O catalysts, the activity (TON) of VO_x species decreased when the vanadium oxide loading was increased from the sub-monolayer to the monolayer content, indicating that the activity of the highly dispersed (isolated and oligomerized) VO_x species is higher than that of the polymeric vanadate. A further decrease of the TON in the supra-monolayer region was due to the formation of bulk vanadium oxide.

The overall selectivity to C_8 oxygenates was a function of both the vanadium oxide loading and of the conversion, which agrees with literature indications. The best selectivity to phthalic anhydride + phthalic acid at high o-xylene conversion was offered by the catalyst well above the monolayer, also containing bulk vanadium oxide, in agreement with the patent literature. On the other hand, the catalyst having the lower amount of vanadium oxide loading (approximately 40% of the monolayer coverage) provided an excellent selectivity to C_8 oxygenates at 50–60% *o*-xylene conversion.

Carrying out the reaction in the presence of 3 vol.% steam in the inlet feed, this amount being higher than that one generated during the reaction, led to a remarkable improvement of catalytic activity. *In situ* Raman measurements evidenced that this effect was due to a dispersion of bulk vanadium oxide to generate a higher number of active sites. This effect was quite reversible, and the interruption of the steam feed led to a recovery of the initial activity and to a re-aggregation of dispersed V species into bulk vanadium oxide.

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