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A revision of the mechanism of *o*-xylene oxidation to phthalic anhydride with V/Ti/O catalysts, and the role of the promoter Cs

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ABSTRACT

This paper describes the effect of Cs oxide, a promoter of an anatase-supported 7 wt.% V_2O_5 catalyst for the oxidation of *o*-xylene to phthalic anhydride. The effect of Cs was investigated in relation to the reaction network at 320 °C, i.e., under conditions of incomplete *o*-xylene conversion. It was found that at this temperature the catalytic performance was affected by a surface-saturation effect. However, Cs had the role of favoring the desorption of intermediates and keeping a cleaner and more oxidizing catalyst surface, so accelerating the conversion of the reactant and the consecutive oxidations occurring upon the reaction intermediates finally leading to phthalic anhydride. This de-saturation derived from the enhancement of the V re-oxidation rate, which is one main effect of Cs in V/Ti/O catalysts. Besides the route of *o*-xylene oxidation to the main reaction intermediate *o*-tolualdehyde, a parallel reaction pathway included the direct oxidation of *o*-xylene to phthalaldehyde; the latter was one intermediate in the formation of phthalide, via intramolecular condensation, and of phthalic acid.

1. Introduction

The selective oxidation of *o*-xylene to phthalic anhydride (PA), catalyzed by titania (anatase)-supported vanadium oxide, has been the object of several investigations in latest decades, and all main aspects concerning the properties necessary to obtain an active and selective V/Ti/O catalyst are well known since long time [1–9]. The research carried out so far has been dealing mainly with the nature of the V species and the interaction that develops between the latter and the titania support, both affecting the catalytic performance. Much less investigated has been the role of promoters, important components of the industrial catalyst [1,10,11]. Promoters playing a fundamental role are Cs, Sb and P, but the patent literature also reports several other elements. The role of promoters is crucial, and the proper control of the relative amount of each component in the catalytic bed, subdivided into several layers having different composition, is fundamental for the process performance. Furthermore, since the reaction network for PA formation is very complex and includes several parallel and consecutive reactions, a proper understanding of the role of each dopant cannot be separated from the analysis of the reaction scheme. This approach, however, has not been used so far for the study of doped V/Ti/O catalysts. In the present work we report the results of an investigation aimed at understanding the role of Cs in V/Ti/O catalysts, in order to evidence in which step of the reaction network does this promoter play its role.

2. Experimental

Two catalysts were prepared using the wet-impregnation technique, (a) an undoped V/Ti/O catalyst containing 7 wt.% V_2O_5, and (b) a Cs-doped V/Ti/O catalyst containing 7 wt.% V_2O_5 and 0.35 wt.% Cs_2O. The surface area of TiO_2 was 22 m^2/g. Samples were calcined in air at 450 °C for 5 h.

For catalytic measurements, a mixture of *o*-xylene vapors in air (either 1 or 0.5 mol% hydrocarbon) was continuously fed to tubular-flow stainless steel reactor operating at atmospheric pressure. Variable amounts of catalysts were loaded in order to carry out tests under isothermal conditions and with variation of the residence time. Some tests were carried out feeding phthalaldehyde vapors; the compound was first dissolved in toluene (concentration 30 mol%), and then the solution was vaporized either in air or in He flow. In both cases, the molar concentration of phthalaldehyde in the feed stream was 0.15%. When tests were made under anaerobic conditions, the toluene/phthalaldehyde mixture was first stripped with He at room temperature for 30 min, in order to remove traces of oxygen. Separate tests were carried out feeding toluene vapors

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either in air or in He; the yield to products so obtained (CO_2, maleic anhydride, benzoic acid) was subtracted from the corresponding yield obtained by feeding the toluene/phthalaldehyde mixture at the same reaction conditions.

3. Results and discussion

3.1. The reaction network

Catalytic tests were carried out with variation of the residence time, at 320 °C, with both the undoped and the Cs-doped V/Ti/O catalysts. Fig. 1 compares the conversion of *o*-xylene and the selectivity to the products. The two catalysts gave the same *o*-xylene conversion up to residence time 0.4 s. However, they showed a great difference for residence time higher than 0.4 s; in fact, the Cs-doped catalyst showed a remarkable increase of conversion, from 34% to 100%, for an increase of 0.1 s residence time only. On the contrary, the undoped catalyst showed an increase of conversion of only the 10% when the residence time was varied from 0.4 to 0.7 s. It is worth mentioning that the experimental trends reported in Fig. 1 were totally reproducible, and were perfectly replicated when the residence time was first increased and then decreased.

With both catalysts, primary products were *o*-tolualdehyde, phthalaldehyde, carbon oxides, phthalic acid, benzoic acid and maleic anhydride. Secondary products were phthalide, *o*-toluic acid and PA. Products that at these conditions underwent consecutive transformations were phthalaldehyde and phthalic acid. The latter, however, showed a minimum selectivity at intermediate values of residence time; this indicates that this compound is also formed by consecutive transformation of a secondary product, most likely PA.

With the undoped catalyst, both phthalide and *o*-toluic acid did not undergo any consecutive reaction, whereas with the Cs-doped catalyst the selectivity to both compounds became nil, and that to PA correspondingly increased, when *o*-xylene reached complete conversion. It is worth noting that the C balance was in all cases comprised between 95% and 102%, even at low *o*-xylene conversion. Therefore, we can exclude the accumulation of heavy compounds on the catalyst surface that were reported to be responsible for the missing C in C balance [3]. The formation of undetected compounds likely occurs only with V/Ti/O catalysts having V_2O_5 content lower than the monolayer.

The reaction network that can be inferred from the experimental results agrees with that one reported in the literature [2–4]; however new aspects, never reported previously, can be proposed. At 320 °C, there are two main direct selective pathways for *o*-xylene transformation. The principal one likely occurs by interaction of the alkylaromatic with the catalyst surface through one methyl group, which is then oxidized to yield *o*-tolualdehyde; the latter compound desorbs into the gas-phase. A less important path occurs by interaction of both methyl groups [3], and oxidation of the hydrocarbon to phthalaldehyde. In fact, both *o*-tolualdehyde and phthalaldehyde are primary products. Unselective parallel reactions of combustion to CO_x, and of formation of maleic anhydride and benzoic acid also occur by oxidative scission of the C–C bond and decarboxylation, and by electrophylic oxidative attack on the aromatic ring of the adsorbed alkylaromatic.

The *o*-tolualdehyde desorbs into the gas-phase and may then re-adsorb and yield *o*-toluic acid. The re-adsorption of phthalaldehyde may yield phthalic acid; the latter, however, is apparently formed by direct reaction, probably because the strong interaction of the dialdehyde with the catalyst surface favors the consecutive oxidation of this compound before it may desorb into the gas-phase. For what concerns the formation of phthalide, this compound is not apparently formed by intramolecular disproportionation and condensation of *o*-toluic acid, but rather seems to form by direct transformation of *o*-tolualdehyde. One possible route from *o*-tolualdehyde to phthalide is by oxidation of the second methyl group and rapid intramolecular Tishchenko-like condensation. The same intramolecular reaction may obviously occur on phthalaldehyde; the low selectivity to this compound experimentally observed is likely due to the fact that the Tishchenko reaction is fast (see tests below).

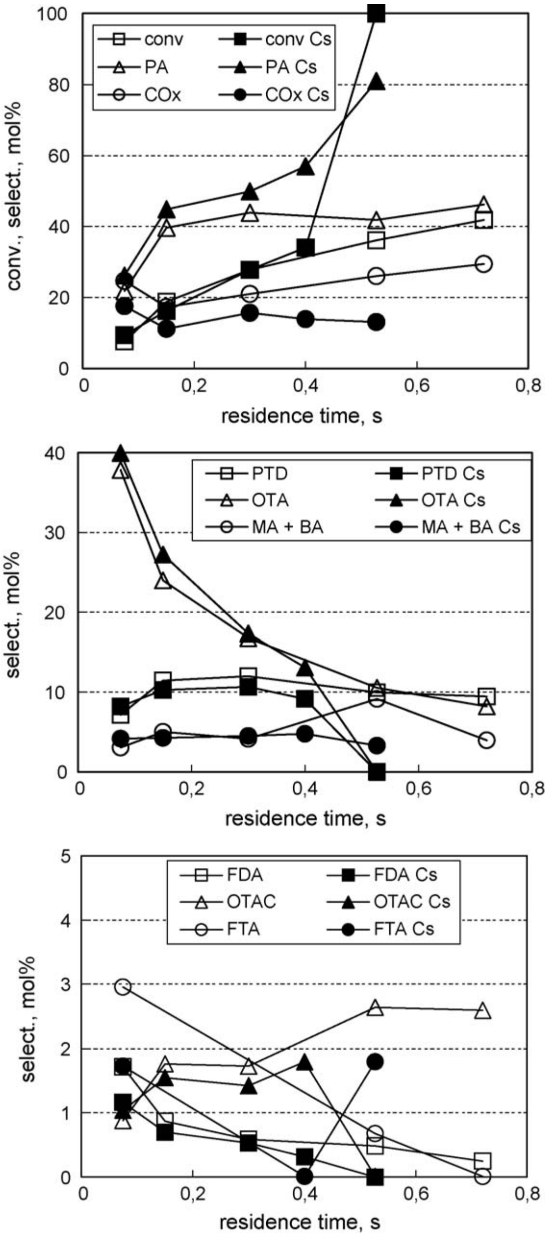

Fig. 1. Conversion of *o*-xylene and selectivity to the products for the undoped V/Ti/O (open symbols) and Cs-doped V/Ti/O (full symbols) catalysts as functions of the residence time. Feed composition: 1 mol% *o*-xylene in air. Temperature 320 °C. PA: phthalic anhydride; PTD: phthalide; OTA: *o*-tolualdehyde; MA: maleic anhydride; BA: benzoic acid; FDA: phthalaldehyde; OTAC: *o*-toluic acid; FTA: phthalic acid.

With the undoped catalyst, phthalide and *o*-toluic acid are not re-adsorbed on the catalyst surface and therefore are not consecutively transformed to PA. Indeed, under these conditions the main route to PA apparently occurs by re-adsorption of *o*-tolualdehyde and direct transformation of this compound. This may occur via oxidation to phthalaldehyde, which may then be transformed through two different pathways, both occurring

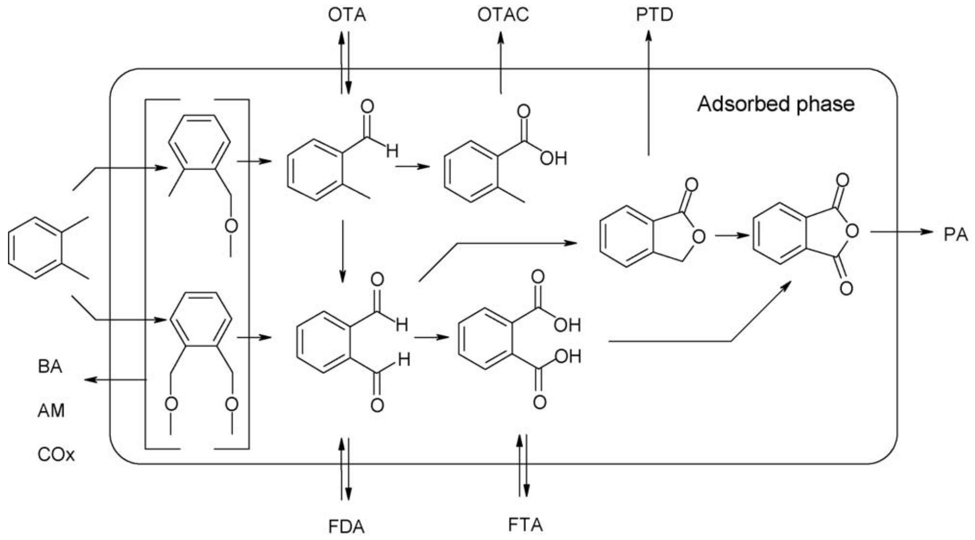

Fig. 2. Reaction scheme of *o*-xylene oxidation catalyzed by V/Ti/O at 320 °C. PA: phthalic anhydride; PTD: phthalide; OTA: *o*-tolualdehyde; MA: maleic anhydride; BA: benzoic acid; FDA: phthalaldehyde; OTAC: *o*-toluic acid; FTA: phthalic acid.

without the desorption of any intermediate compound: (a) the oxidation of the dialdehyde to phthalic acid, which then dehydrates to PA, and (b) the intramolecular condensation to yield phthalide, which is then oxidized to PA. The former reaction may give the greater contribution, as suggested by the fact that gas-phase phthalide does not interact (i.e., is not re-adsorbed) with the catalyst under these conditions. Fig. 2 summarizes the reaction network under conditions of incomplete *o*-xylene conversion, as inferred from results obtained at 320 °C.

3.2. The role of the dopant Cs

One major result of catalytic tests is that the undoped catalyst works at a surface-saturation state, i.e., at conditions of maximal coverage of the surface with the organic reactant and the intermediates. This is demonstrated by the trend of the *o*-xylene conversion in function of the residence time; moreover, the re-adsorption and oxidation of gas-phase phthalide and *o*-toluic acid is hindered likely because of the scarceness of oxidizing sites available on the catalyst surface at 320 °C. The main role of Cs, therefore, is to maintain a cleaner and more oxidized active surface, by accelerating the re-oxidation of reduced V sites and hence by favoring the desorption of intermediate compounds and their re-adsorption and consecutive oxidation to PA. This agrees with the role of Cs in doped V/Ti/O catalysts, which was found to accelerate the catalyst re-oxidation by O_2 [10,11]. In fact, it was found that with the Cs-promoted catalyst the rate-determining step of the reaction is vanadium re-oxidation; moreover, TPR/TPO measurements evidenced that the presence of increasing amounts of Cs enhanced the rate of the rate-determining step, accelerating the re-oxidation of reduced V sites by O_2.

The Cs effect however becomes evident at 320 °C only when *o*-xylene conversion is higher than the 30%. This is likely due to the fact that an increase of the hydrocarbon conversion causes an increase of the O_2/*o*-xylene ratio in the gas-phase; only when this ratio becomes higher than a defined value, does the enhancement effect of Cs on V re-oxidation rate become effective and play a role on catalytic performance. If this hypothesis is true, we should observe no activity enhancement effect by Cs when a hydrocarbon-leaner feedstock is used, that is under conditions at which the surface concentration of reactants and intermediates is lower. In order to confirm this, we repeated the catalytic measurements by feeding a mixture containing 0.5% *o*-xylene vapors in air; the results are summarized in Fig. 3. It is shown that the two catalysts gave the same conversion, and that under these conditions all the reaction intermediates were re-adsorbed and successively oxidized to PA. With the undoped catalyst, the conversion of *o*-xylene at 0.15 s and at 0.45 s residence time, with *o*-xylene-lean conditions, was much greater than that observed with 1% *o*-xylene in feed. This clearly indicates that under the latter conditions the catalyst surface is saturated by the adsorbed reactant and intermediates.

The Cs-doped catalyst showed to be more selective to PA at all conversion levels, at both conditions of inlet *o*-xylene concentration tested. This corresponded to a lower selectivity to CO_x, even at very low *o*-xylene conversion. The other consecutive transformations were apparently not affected by the presence of Cs. This indicates that the higher availability of surface oxidizing sites favors the selective oxidation of adsorbed *o*-xylene, and lowers the contribution of parallel combustion by non-selective oxygen species.

One reaction supposed to play a role in the reaction network, at least at 320 °C, is the intramolecular Tishchenko-like condensation of phthalaldehyde to phthalide. This reaction occurs over basic catalysts [12,13], whereas it has never been reported to occur in the gas-phase with vanadia-based catalysts. Therefore, in order to demonstrate the possible role of this step in the reaction network for PA formation, we carried out tests with both the undoped and the Cs-doped catalyst, by feeding phthalaldehyde vapors in a He stream (see Section 2 for the detailed description of the tests). Fig. 4 reports the effect of time-on-stream on phthalaldehyde conversion and on selectivity to the products, for the Cs-doped catalyst. The result obtained with the undoped catalyst at the beginning of the reaction time is also reported.

Under anaerobic conditions, both catalysts converted phthalaldehyde; the products were phthalide, PA and benzoic acid; also traces of *o*-tolualdehyde and *o*-toluic acid were found. CO_x formed only with the undoped V/Ti/O. The activity declined during the first hours of reaction, until a stable performance was reached after approximately 8 h reaction time. This behavior may be attributed to the fact that under anaerobic conditions, the bulk oxygen was progressively consumed to oxidize phthalide into PA; on the contrary, the transformation of phthalaldehyde into phthalide does not require any additional oxygen input. However, the overall selectivity to phthalide and PA, the two main products, remained

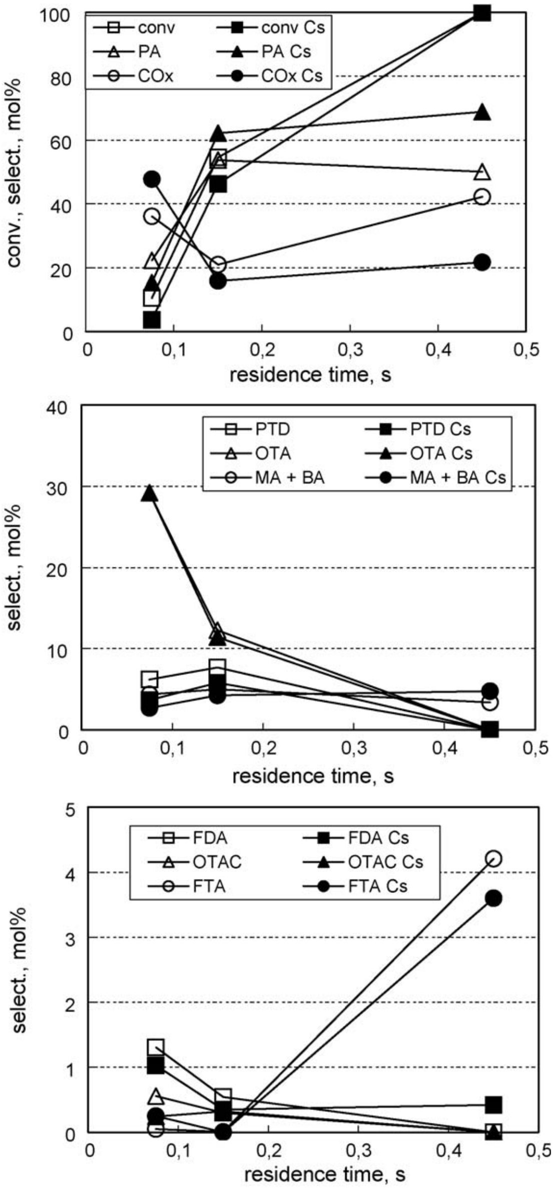

Fig. 3. Conversion of *o*-xylene and selectivity to the products for the undoped V/Ti/O (open symbols) and Cs-doped V/Ti/O (full symbols) catalysts as functions of the residence time. Feed composition: 0.5 mol% *o*-xylene in air. Temperature: 320 °C. Symbols as in Fig 1.

approximately unchanged during the reactivity tests. Therefore, the possible presence of traces of O_2 in feed is likely, although care was taken to avoid it in the reactor inlet stream (see Section 2).

Some differences were shown between the two catalysts in phthalaldehyde transformation. At the very beginning of the reaction time, the undoped catalyst was more active than the Cs-doped one, and was more selective to PA and less selective to phthalide. However, with both catalysts the latter compound was the main reaction product. Moreover, the undoped system produced CO_x that was instead not produced at all with the Cs-doped catalyst. These data indicate that under anaerobic conditions the undoped catalyst was a stronger oxidant than the Cs-doped one; this result is in agreement with what previously reported [10,11], that the addition of Cs to the V/Ti/O catalysts decreases the V^{5+} reducibility.

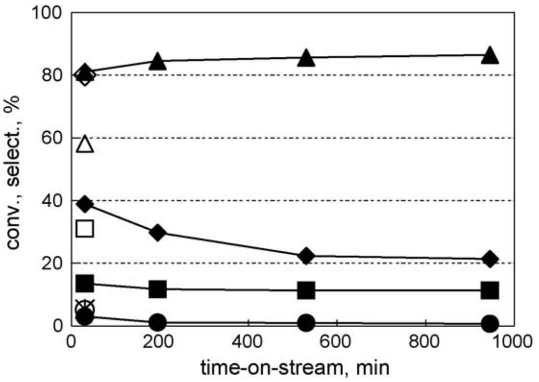

Fig. 4. Conversion of phthalaldehyde (◆◇), selectivity to phthalide (▲△), to phthalic anhydride (■□), to benzoic acid (●○) and to CO_x (*) as a function of time-on-stream under anaerobic conditions. Open symbols: undoped V/Ti/O catalyst; full symbols: Cs-doped V/Ti/O catalyst. Feed composition: 0.15 mol% phthalaldehyde, 0.50 mol% toluene, remainder He. Residence time 0.3 s. Temperature: 320 °C.

When air was also fed (results not reported), with both catalysts the conversion of phthalaldehyde was total already at 230 °C. PA was the main product, formed with selectivity higher than 90% at temperature lower than 270 °C, and of 83–87% between 270 and 320 °C. Other by-products were phthalide and CO_x; benzoic acid and maleic anhydride formed with the undoped catalyst, whereas these compounds did not form with the Cs-doped catalyst.

4. Conclusions

The effect of the dopant Cs on the catalytic performance of a titania (anatase)-supported 7 wt.% V_2O_5 catalyst in *o*-xylene oxidation to PA has been investigated in relation to the reaction network at 320 °C, i.e., under conditions of incomplete hydrocarbon conversion. It was found that the catalytic performance is affected by a surface-saturation effect; in fact, under these conditions the conversion of *o*-xylene and the consecutive oxidation of intermediates *o*-toluic acid and phthalide was inhibited. However, Cs played the role of maintaining a cleaner and more oxidizing catalyst surface, but only under those conditions at which the increase of *o*-xylene conversion caused a corresponding increase of the gas-phase O_2/hydrocarbon molar ratio. This de-saturation derived from the enhancement of the V re-oxidation rate, which is one main effect of Cs in V/Ti/O catalysts [10]. A parallel reaction pathway included the direct oxidation of *o*-xylene to phthalaldehyde; the latter was one intermediate in the formation of phthalide, via intramolecular condensation, and of phthalic acid as well.

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