Facile and not facile reactions for the production of maleic and phthalic anhydrides with vanadium mixed oxides based catalysts

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Vanadium is a key element in the formulation of catalysts for the production of anhydrides by selective vapor oxidation with molecular oxygen. A study of the oxidations of *o*-xylene, *n*-butane and benzene on V–P, V–Mo and V–Ti mixed oxides, the commercial catalysts for the synthesis of anhydrides, was carried out. The oxidation of *o*-xylene on the three catalysts was the most facile reaction leading to high yields in phthalic anhydride; on the contrary in the oxidation of *n*-butane only V–P mixed oxide was active and selective. V–P mixed oxide is active and selective in the oxidation of all the feedstocks and can be identified as the most polyfunctional catalyst. V–Mo is active and selective in both *o*-xylene and benzene oxidation and V–Ti only in *o*-xylene oxidation. Moreover the lesser selectivity in phthalic anhydride observed with V–P and V–Mo mixed oxides has been attributed to parallel oxidation reactions to the formation of phthalic anhydride, evidenced by a higher amount of phthalide.

Keywords: Butane oxidation; benzene oxidation; *o*-xylene oxidation; vanadium based catalysts; maleic anhydride; phthalic anhydride.

1. Introduction

Vanadium is a key element in the formulation of catalysts utilized in the production of anhydrides via selective oxidation reactions in vapor phase with molecular oxygen. The following different partners in industrial catalysts for anhydride production are presently being used:

– V_2O_5 supported on TiO_2 in the oxidation of *o*-xylene and naphthalene to phthalic anhydride (indicated as V-Ti),

– V_2O_5–MoO_3 in the oxidation of benzene to maleic anhydride (indicated as V-Mo),

– V_2O_5–P_2O_5 in the oxidation of *n*-butane to maleic anhydride (indicated as V-P).

There is a good agreement in the literature regarding the catalytic phases responsible for the industrial reactions. In the V-P system $(VO)_2P_2O_7$ has been identified as the only phase present (with traces of V(V) and V(III))[1–7]. In the V-Ti system V_6O_{13} or V_3O_7 [8–12] has been proposed as the active and selective phase in the oxidation of o-xylene to phthalic anhydride. In the V-Mo system the proposed active phase in the oxidation of benzene to maleic anhydride is a V_2O_5–MoO_3 solid solution which after reduction becomes $(V_{0.66}Mo_{0.33})_6O_{13}$, probably the real active phase [12–14]. Therefore it seems that the role of several partners in industrial catalysts is to stabilize a different valence state of vanadium and that each reagent requires a different optimal concentration of the different valences of vanadium.

It is not easy to find comparable data in the literature on the activity of the above three types of catalysts for reactions different from those where they are industrially applied and in particular for different raw materials or other anhydrides.

The aim of this study was to evaluate the catalytic behavior of the three optimized catalytic systems in o-xylene, benzene and n-butane oxidation, with the specific objective of accumulating comparable activity data that can help to build a suitable model to provide better predictions regarding selectivity in the oxidation of hydrocarbons on mixed oxide based catalysts.

2. Experimental

V_2O_5–TiO_2 has been synthesized according to the method described in patent [15]. TiO_2 anatase has been impregnated with a solution of vanadyl oxalate and KCl, obtaining $TiO_2/V_2O_5/KCl$ mass ratio of 212/11/1 and calcined at 390°C for 9 h.

V-Mo mixed oxides have been prepared according to the method described in patent [16] by evaporation of a solution containing 6 parts (by weight) of ammonium paramolybdate, 13.22 parts ammonium metavanadate, 71.43 parts of hydrochloric acid and Ni, Bi, Na phosphate.

The composition of calcined catalyst by weight is: 1 part of MoO_3, 2.1 parts of V_2O_5, 0.03 parts of P_2O_5, 0.04 parts of Na_2O, 0.04 parts of NiO and 0.06 parts of Bi_2O_3.

Vanadyl pyrophosphate, the active phase of the V_2O_5–P_2O_5 catalyst, was prepared according to the organic method proposed in several papers [1,17–19]. In a typical preparation V_2O_5 was reduced in a 2 : 1 = isobutanol : benzyl alcohol mixture under reflux conditions. The solution, containing vanadium in oxidation state III, was cooled and an exact amount of orthophosphoric acid 100% was added under nitrogen flow. The blue suspension obtained was filtered and dried. Finally the sample was calcined in air and then in n-butane/air mixture.

The catalysts were initially activated and studied in their industrial applications until steady-state conditions were reached:

– V_2O_5 supported on TiO_2 in the oxidation of *o*-xylene to phthalic anhydride (surface area $15 \, m^2/g$),

– V_2O_5–MoO_3 in the oxidation of benzene to maleic anhydride (surface area $17 \, m^2/g$),

– V_2O_5–P_2O_5 in the oxidation of *n*-butane to maleic anhydride (surface area $25 \, m^2/g$).

The catalyst weights were 1 g for V-Ti, 4 g for V-P and 2 g for V-Mo. The dimensions of particles and of the inert were 0.42–0.60 mm. The amount of catalyst has been chosen in order to achieve about the same conversion of *o*-xylene at low temperature. Steatite was added to the catalyst in order to minimize the temperature gradient effect. The catalyst/steatite ratio was 1 : 4 (w/w). The catalytic experiments were run in a fixed bed reactor loaded with the catalyst/steatite mixture. The reactants were fed in an air flow of 60 ml/min. The hydrocarbon concentrations were fixed in the following values: 1.1% for *o*-xylene, 1.3% for benzene and 1.0% for *n*-butane (the values are given in molar amount).

The products were analyzed using an off-line system consisting of a crystallizer and two acetone absorbers. The products were concentrated for 1 h and then analyzed using a gas-chromatograph with a FID detector. Permanent gases were analyzed with a TCD gas-chromatograph.

3. Results and discussion

3.1. CONVERSION AND ANHYDRIDE PRODUCTION

The reaction temperatures at 30, 60 and 90% of conversion for each catalyst and for the three reactions investigated are reported in table 1. The following scale of activity can be deduced from the results reported in table 1:

o-xylene oxidation   V-Ti $\approx$ V-Mo $\approx$ V-P
benzene oxidation   V-Mo $\gg$ V-P $\gg$ V-Ti
n-butane oxidation   V-Mo $>$ V-P $\gg$ V-Ti .

Table 1
o-xylene, benzene and *n*-butane reaction temperatures at 30, 60 and 90% of conversion on the three catalytic systems. Reaction parameters: flow rate: 60 ml/min, amount of catalysts: V-Ti = 1 g, V-Mo = 2 g, V-P = 4 g

	Reaction temperature (°C) at 30% conversion			Reaction temperature (°C) at 60% conversion			Reaction temperature (°C) at 90% conversion		
	V-Ti	V-Mo	V-P	V-Ti	V-Mo	V-P	V-Ti	V-Mo	V-P
o-xylene	303	306	308	322	325	330	341	345	347
benzene	420	294	347	–	311	375	–	320	405
n-butane	410	314	330	–	354	360	–	398	390

The oxidation of *o*-xylene has been chosen as reference for the evaluation of other reactions. Thus different amounts of catalyst have been used in order to achieve paragonable conversion of *o*-xylene. However, the real scale of activity per weight of catalyst in the oxidation of *o*-xylene is V/Ti > V/Mo > V/P (taking in account the activity per gram of vanadium this scale is again followed). The maximum yields in phthalic and maleic anhydride versus the feed supplied on the three different catalysts are plotted in fig. 1.

From table 1 and fig. 1 it is possible to observe that at the chosen reaction conditions the three catalytic systems are active and selective in *o*-xylene oxidation to phthalic anhydride in the same range of temperatures (maximum phthalic anhydride yield detected at 350–365°C). V-Ti was the most selective catalyst but the other two catalysts also gave very high amounts of phthalic anhydride. In the *n*-butane and benzene oxidation, the activity of V-Ti was very low in the range of temperatures investigated. In the *n*-butane oxidation only V-P was found active and selective in maleic anhydride production while V-Mo was active but not selective. In the oxidation of benzene, V-Mo gave high yield in maleic anhydride, but the V-P system also gave an interesting yield mainly in maleic but also in phthalic anhydride.

Considering the data in fig. 1 it is evident that oxidation of *n*-butane is a reaction which accentuated the differences among the catalysts. In other words the transformation of *n*-butane to maleic anhydride is more "structure-sensitive" and requires a more sophisticated type of catalyst. On the contrary, *o*-xylene oxidation is the most *facile* reaction and *o*-xylene can be converted to phthalic anhydride by a wide range of oxides. In addition, if we consider that V-P catalyst is also able to give
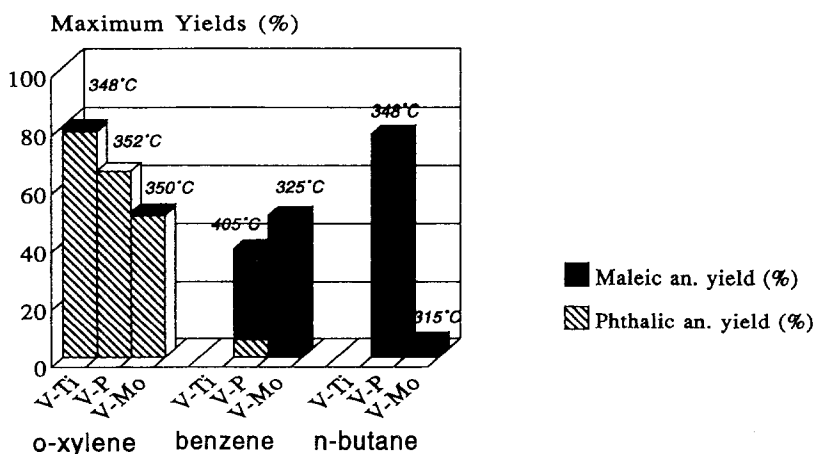

Fig. 1. Maximum yields in maleic and phthalic anhydrides as a function of the feed and of the catalyst. Flow rate: 60 ml/min, catalyst amount: V-Ti = 1 g, V-Mo = 2 g, V-P = 4 g.

interesting anhydride yields with all feeds, it can be regarded as the most polyfunctional type of catalyst.

These conclusions are in agreement with the mechanism proposed for oxidation of n-butane to maleic anhydride where a wide range of reactions takes place:

butane → butene	oxidative dehydrogenation
butene → butadiene	allylic oxidation
butadiene → 2,3-dihydrofuran	1-4 oxygen insertion
2,3-dihydrofuran → furan	allylic oxidation
furan → maleic anhydride	electrophilic oxygen insertion

The center responsible for hydrogen extraction from the methyl group in o-xylene can be considered similar to the allylic hydrogen abstraction of an olefin, while the oxygen insertion in benzene can be considered similar to the 1-4 oxygen insertion in butadiene.

V-Ti has an insufficient number of sites able to give dehydrogenation of paraffins and 1-4 oxygen insertion at temperature less than 400°C.

3.2. NATURE OF THE BY-PRODUCTS

Further differences among three catalysts were observed in by-products. The discussion here is focused on the nature of the by-products in o-xylene oxidation, the only reaction where all the catalysts were found to be active and selective. Percent conversion, phthalic anhydride and by-product yields for all the catalysts are reported in table 2 as a function of the temperature in the o-xylene oxidation. V-P and V-Mo, the less selective catalysts, gave phthalide and traces of o-tolualdehyde from low conversion till relatively high conversion while V-Ti gave only traces of phthalide at very low conversion. Maleic anhydride was found only on V-Ti catalyst and on V-Mo catalyst at higher conversion.

Phthalic anhydride selectivities as a function of the percent conversion are
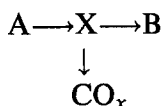
Table 2
o-xylene oxidation distribution products (%) as a function of temperature. Reaction parameters: flow rate: 60 ml/min, amount of catalysts: V-Ti = 1 g, V-Mo = 2 g, V-P = 4 g [a]

T (°C)	V-Ti				V-P				V-Mo				
	C	PA yield	MA yield	CO + CO$_2$ yield	C	PA yield	Pd yield	CO + CO$_2$ yield	C	PA yield	Pd yield	MA yield	CO + CO$_2$ yield
300	25	17	0.0	5	18	13	2.4	3	25	11	1.2	0.0	12
315	49	35	0.6	11	38	28	3.4	7	45	21	2.3	0.0	20
330	73	57	0.9	15	64	40	–	20	67	35	2.8	0.0	30
345	96	78	1.2	16	90	60	–	29	90	46	2.2	0.6	40
360	100	75	1.6	23	100	70	–	30	100	44	0.2	1.5	53
375	100	70	1.7	28	100	65	–	35	100	24	0.0	2.4	74

[a] C = conversion (%), PA = phthalic anhydride, MA = maleic anhydride, Pd = phthalide.

reported in fig. 2. The data show that selectivities do not depend on conversion and this indicates the high stability of phthalic anhydride (this behaviour has been also observed by increasing the contact time at 340°C) as well as that combustion products, which derive from a parallel reaction to the formation of anhydride, present analogous activation energy of the main reaction. A possible parallel reaction is the attack on the aromatic ring with the formation of maleic anhydride, but this reaction must be excluded for less selective catalysts because maleic anhydride is not observed on V-P catalyst, and it is observed only at high conversion on V-Mo catalyst. Therefore combustion products would be derived mainly by parallel reaction starting from intermediates which can be more reactive than raw materials:

$$A \longrightarrow X \longrightarrow B$$
$$\downarrow$$
$$CO_x$$

Phthalide, observed in the oxidation of o-xylene on less selective catalysts (table 2), has been proposed as intermediate. This thesis is true but probably insufficient to explain the entire mechanism of phthalic anhydride formation which probably derives from two parallel reactions, as proposed in the model given in fig. 3.

In the first route the formation of a diacid facilitated the condensation to phthalic anhydride with little decarboxylation. We hypothesize that in V-Ti catalyst the first route is more favourable, leading to a more selective reaction. For the second route we propose that only two vanadium species are involved (a situation which is present in $VO_2P_2O_7$ [6]), o-tolualdehyde and phthalide are formed and they can
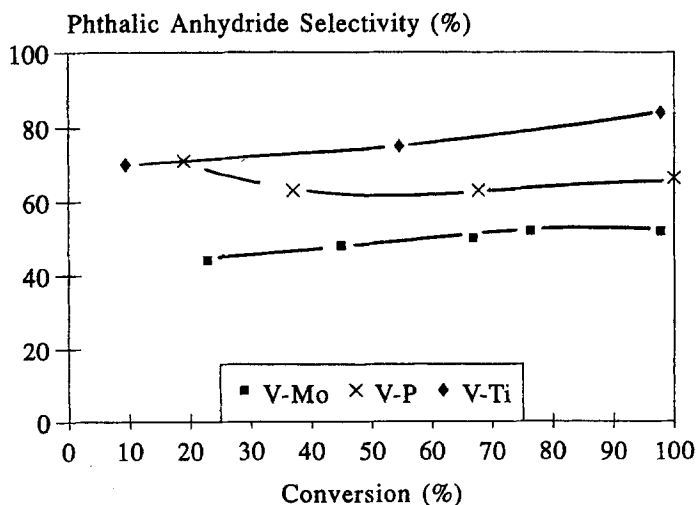
Phthalic Anhydride Selectivity (%)

Fig. 2. Selectivity in phthalic anhydride as a function of the conversion in the oxidation of o-xylene on the three catalysts. Flow rate: 60 ml/min, catalyst amount: V-Ti = 1 g, V-Mo = 2 g, V-P = 4 g.
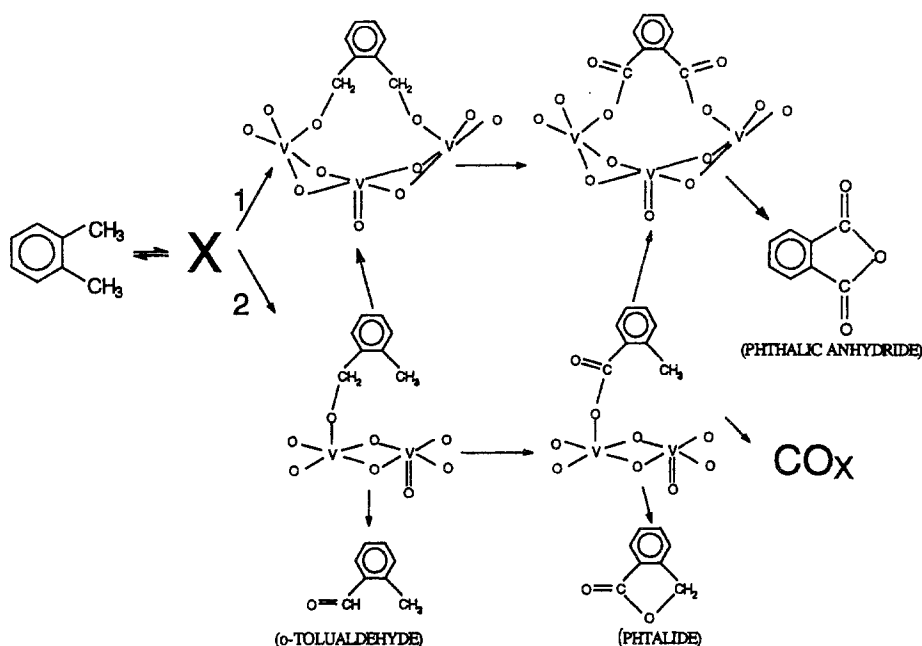
Fig. 3. Proposed model for the formation of phthalic anhydride.

evolve to phthalic anhydride but also to CO_x. In fact the detection of a higher amount of phthalide is an indication of the oxidating attack on a single methyl group. While the single acid can very easily decarboxylate before oxidation on the second methyl group, the diacid can be more quickly condensed to stable phthalic anhydride. V-Mo and V-P catalysts are less selective because the second route is competitive and this may be due to the fact that vanadium sites are more diluted than on V-Ti mixed oxides where TiO_2 acts only as a support.

In conclusion the different selectivities of the catalysts are not related to the different rates of degradation of phthalic anhydride and to the different abilities of oxidative addition to the aromatic ring, but very likely to different reaction pathways and/or different reactivities of the intermediate products formed, in particular the contemporaneous oxidating attack on the two methyl groups (the selective route) in alternative to an oxidation to a single methyl group (as evidenced by the detection of the higher amount of phthalide as by-product).

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