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Non-steady catalytic performance as a tool for the identification of the active surface in VPO, catalyst for *n*-butane oxidation to maleic anhydride

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Abstract

The reactivity of equilibrated VPO catalysts with different P/V ratio was investigated under steady and unsteady conditions, with the aim of gaining information on the status of the active surface in reaction conditions. Specific treatments were applied, and then the unsteady performance was followed along with the reaction time, until the steady behaviour was recovered. These transient states made possible to infer that the nature of the true active surface is a function of the VPO characteristics and of the reaction conditions. With the catalyst having P/V ratio >1.0, the hydrolysis of the VPP surface under working conditions at temperatures higher than 340–350 °C, followed by the oxidation of vanadium, generates an active layer made of vanadium oxide and of P_2O_5/H_2O. When instead the P/V ratio is close to 1.0, the VPP surface is oxidized to $VOPO_4$ already at mild temperature under working conditions, with development of an active layer which is very active but unselective to maleic anhydride at 380 °C. Higher temperatures then lead to the hydrolysis of $VOPO_4$, with generation of an active layer which is similar, and behaves similarly, to that one which develops with the catalyst having P/V ratio >1.0.

Keywords: Vanadyl pyrophosphate; Maleic anhydride; *n*-Butane oxidation; Vanadium phosphate

1. Introduction

The industrial catalyst for *n*-butane oxidation is a vanadium/phosphorus mixed oxide (VPO), in which bulk vanadyl pyrophosphate (VPP), $(VO)_2P_2O_7$, is the main component. The nature of the active surface in VPP has been studied by several authors, often with the use of in situ techniques [1–5]. Several articles discuss the role of different crystalline and/or amorphous VPO compounds, in the complex transformation of the alkane to MA [6–9]. Different hypothesis were formulated; while bulk VPP is in all cases assumed to constitute the core of the active phase, differences concern the nature of the first atomic layers, those that are in direct contact with the gas phase. It is well known that surface reconstruction, especially in the presence of reactive gases, may substantially alter the surface arrangement of atoms as compared to the bulk. However, due to the difficulties in getting information under reaction conditions on the catalytically active surface, the alternative hypothesis either indicate the development of surface amorphous layers which play a direct role in the reaction [10–14], or are based on the crystallographic models of the VPP, assuming that specific planes contribute to the reaction pattern [2,15–21], and that the redox process occurs reversibly between VPP and $VOPO_4$ [3,22].

An excellent discussion of the scientific literature dealing with the working state of the active surface in VPP has been recently published by Schlögl and co-workers [23]. The discussion is supported by in situ measurements of the structure of the active compound and of the composition of the surface [24,25]. HRTEM images of basal and prism edges of the VPP made possible the identification of non-crystalline adlayer, about 1 nm thick, on the surface of equilibrated VPO catalysts [23]. By application of in situ X-ray absorption spectroscopy (XAS) and

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in situ XPS, it was concluded that the working surface is a two-dimensional structure containing more O than that present in the VPP; it is originated in situ by hydrolysis of the VPP, which is metastable under reaction conditions [26]. The authors viewed this surface layer as being constituted of a binary VO_y, the growth of which is hindered by phosphate groups [23–25]. This is different from the development of the thick layers of amorphous phases or from segregation of $VOPO_4$, detrimental for catalytic performance, which are more typical of fresh or non-equilibrated catalysts. In contrast with this hypothesis are the results reported by Guliants et al. [27]; the authors found by means of in situ Raman and XRD techniques that a disordered layer about 2 nm thick, covering the surface (1 0 0) planes of fresh VPP, disappeared during equilibration yielding a crystalline solid with steady and optimal catalytic performance.

Therefore, it is evident that despite the many in situ techniques employed for the investigation of VPP, it is not possible to draw a general picture concerning the nature of the active phase in VPP under working conditions. One possible explanation, which was the starting point for our research activity, is that the nature of the active phase that develops is a function of reaction conditions, and of the main features of VPO catalysts. Amongst the latter, the P/V atomic ratio is known to play an important role. With this in mind, we prepared three different catalysts having P/V ratio of 0.99, 1.03 and 1.15, and investigated the catalytic performance after catalyst equilibration had been reached.

2. Experimental

Catalysts were prepared by the ‘‘organic procedure’’ for the synthesis of $VOHPO_4 0.5H_2O$, the precursor of VPP. This preparation consists in the suspension of the desired amounts of V_2O_5 and H_3PO_4 in isobutanol. The precipitate finally obtained is then thermally treated according to the following procedure: (a) drying at 120 °C for 12 h, in static air; (b) pre-calcination step in flowing air, with temperature gradient from room temperature up to 300 °C; then isothermal step at 300 °C in air for 6 h; (c) calcination step in flowing N_2, with temperature gradient from 300 to 550 °C, and final isothermal step at the latter temperature for 6 h. Three samples were prepared, having P/V ratio equal to 0.99, 1.03 and 1.15; the atomic P/V ratio in precursors was confirmed by means of SEM-EDX.

Catalytic tests were carried out in a laboratory glass flow-reactor, loading 0.8 g of catalyst. Products were analyzed by means of gas chromatography (on-line sampling of exit stream), equipped with a HP-1 column for the separation of C4 hydrocarbons, formaldehyde, acetic acid, acrylic acid, maleic anhydride. A Carbosieve SII column was used for the separation of oxygen, carbon monoxide and carbon dioxide.

3. Results and discussion

3.1. Steady-state catalytic performance of equilibrated VPO catalysts

Fig. 1 plots the effect of temperature on *n*-butane conversion, and on the selectivity to maleic anhydride, for three catalysts having P/V atomic ratio equal to 0.99, 1.03 and 1.15. It is worth noting that preliminarily to these tests, catalysts were maintained for 150 h at 400 °C with the reaction stream, and that after this period they can be considered as ‘‘equilibrated’’ or almost equilibrated ones. In fact, they did not exhibit any further variation of catalytic performance along with the increasing reaction time. It is also useful to remind that for these equilibrated catalysts, the performance shown in Fig. 1 was completely reversible, that is, the curves were fully reproduced when the temperature was raised and lowered in sequence several times. This is the starting point of our investigation; trends shown in Fig. 1 were not due to irreversible modifications of the catalysts, and did not occur as a consequence of the ongoing equilibration of the samples.

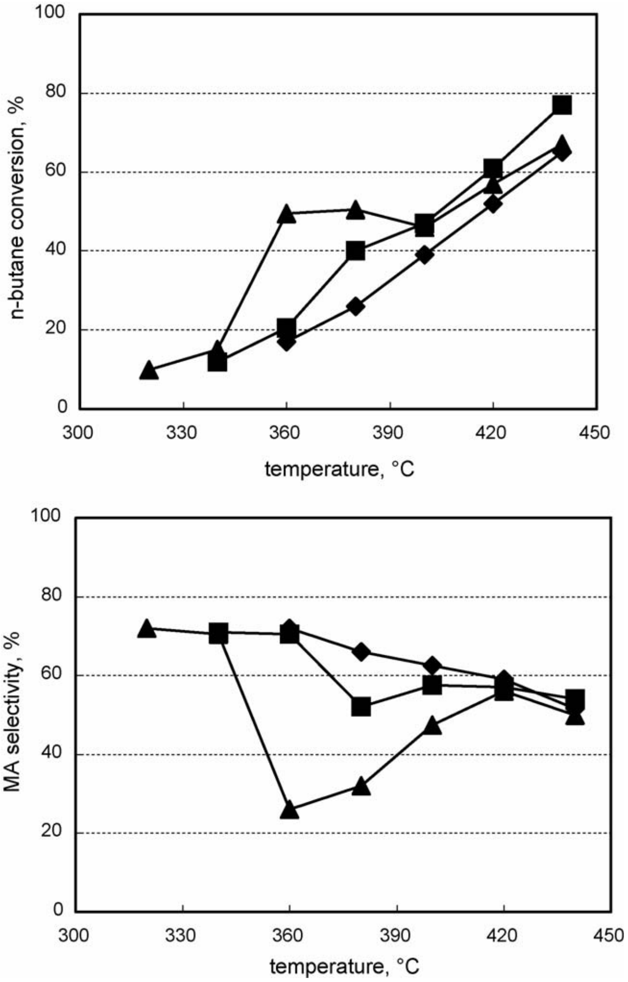

Fig. 1. Conversion of *n*-butane (top) and selectivity to maleic anhydride (bottom) as functions of the reaction temperature for catalysts having P/V = 0.99 (▲), 1.03 (■) and 1.15 (◆).

Results in Fig. 1 demonstrate that the P/V ratio greatly affected the catalytic performance. While the sample having excess P had the expected trend for both *n*-butane conversion and selectivity to maleic anhydride, the one having P/V 0.99 gave a jump of activity at 340–350 °C, which was then recovered at temperatures higher than 370–380 °C. The sample with P/V = 1.03 showed a catalytic behaviour which was intermediate between those of samples with P/V = 0.99 and

1.15. Therefore, while the three catalysts had comparable activity at low and high temperature, they differed considerably in the intermediate temperature range. The same occurred with the selectivity to maleic anhydride: the catalyst having P/V = 0.99 showed a fall of selectivity in correspondence of the activity increase; this fall was then recovered above 360 °C. It is worth noting that the decrease of selectivity was not simply due to the increase of conversion; in fact, "good" VPO catalysts giving 50% *n*-butane conversion at 380 °C, produce maleic anhydride with selectivity higher than 50% [7].

The experimental effects are attributable to reversible modifications in the nature of the active surface, the occurrence of which was a function of the reaction temperature; these modifications were particularly evident in the sample having P/V = 0.99. We assumed that these phenomena can be studied through the analysis of these reversible transitions, and that the latter can be forced by inducing transient changes, through the application of treatments of oxidation and hydrolysis aimed to the modification of the active surface characteristics.

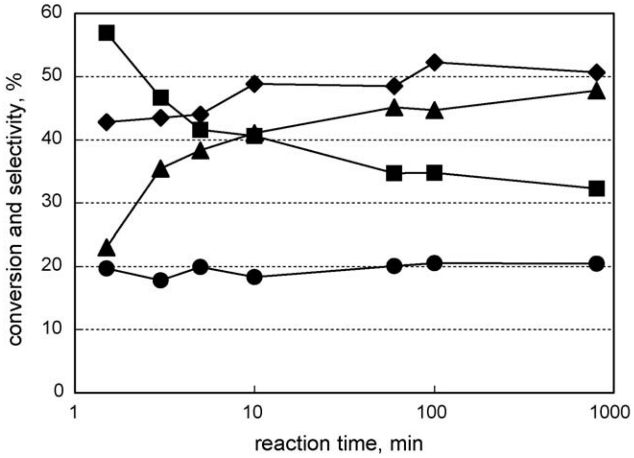

Fig. 2. Conversion of *n*-butane (◆), selectivity to maleic anhydride (■), to carbon oxides (▲), and to formaldehyde plus acetic acid plus acrylic acid (●) as functions of the reaction time during Test 3a of Table 1.

3.2. Non-steady catalytic performance of equilibrated VPO catalysts

We forced transient states, by applying conditions different from those the catalyst underwent under reaction. Specifically, we chose three representative temperatures: 320–340, 380 and 440 °C, and at each temperature level we induced modifications in the stable active surface by applying either oxidizing treatments (feed of air), or hydrolyzing treatments (feed of 4% steam in He). Then, we fed again the reaction mixture, and followed the variation of catalytic performance that occurred

Table 1
Description of tests run with catalyst having P/V = 0.99

Test no	Conditions for tests, T and feed[a]	Initial performance in step c[b]	Final performance in step c[b] (time)[c]	Information gained
1a	(a)–, (b) 200 → 320 °C, in He, (c) 320 °C, mix	X 9, ∅ 72	X 9, ∅ 72	Heating in He does not alter the active surface at 320 °C.
2a	(a) 320 °C, mix, (b) 320 → 380 °C, in He, (c) 380 °C, mix	X 51, ∅ 31	X 51, ∅ 31	The active surface is the same at 320 °C and at 380 °C.
3a	(a) 440 °C, mix, (b) 440 °C → 380 °C, in He, (c) 380 °C, mix	X 43, ∅ 57	X 51, ∅ 32, (8–10 h)	The active surface which forms at 440 °C is less active but much more selective than that one which forms at 380 °C.
4a	(a) 320 °C, mix, (b) 320 °C, air, 2 h, (c) 320 °C, mix	X 10, ∅ 72	X 10, ∅ 72	The active surface at 320 °C is not altered by a treatment in air; therefore, the active surface is in the higher oxidation state for these conditions.
5a	(a) 380 °C, mix, (b) 380 °C, air, 1 h, (c) 380 °C, mix	X 53, ∅ 32	X 51, ∅ 32	The active surface at 380 °C is not altered by a treatment in air; therefore, the active surface is in the higher oxidation state for these conditions.
6a	(a) 380 °C, mix, (b) 380 °C, 4% H_2O in He, 1 h, (c) 380 °C, mix	X 44, ∅ 41	X 53, ∅ 29, (2 h)	At 380 °C, the hydrolysis renders the active surface less active and more selective.
7a	(a) 380 °C, mix, (b) 380 °C, 4% H_2O in air, 1 h, (c) 380 °C, mix	X 55, ∅ 38	X 56, ∅ 30, (1.5 h)	The hydrolysis (test 6a) renders the catalyst oxidizable, and this makes the active surface slightly more selective.
8a	(a) 440 °C, mix, (b) 440 °C, air, 1 h, (c) 440 °C, mix	X 69, ∅ 47	X 67, ∅ 50	The active surface at 440 °C is not substantially altered by an oxidative treatment at 440 °C. Therefore, the active surface is in the higher oxidation state for these conditions.
9a	(a) 440 °C, mix, (b) 440 °C, 4% H_2O in He, 1 h, (c) 440 °C, mix	X 67, ∅ 46	X 65, ∅ 48	The active surface at 440 °C is not substantially altered by an hydrolysis treatment at 440 °C. Therefore, the active surface is already hydrolysed under these conditions.

[a] (a): Steady performance with the reaction mixture (mix); (b): Treatment; (c) unsteady performance with the reaction mixture (mix).

[b] *X* = *n*-butane conversion, %; ∅ = selectivity to maleic anhydride, %.

[c] Time necessary to reach the steady final performance in step c, hours. If not indicated, the performance was stable all along step c.

along with time-on-stream, during the transition of the catalyst from the forced situation to that one stable under those conditions. The steady state finally corresponds to that one which is reported, for each temperature level, in Fig. 1.

In most cases, variations were slow and could be followed along reasonable periods of time, e.g., of a few hours. When the treatment induced no variation in catalytic performance, we assumed that either the active surface was stable towards that treatment, or that it was insensitive to it, because it was already in the state we were meant to induce by that specific treatment. Other tests were made by changing the reaction temperature in He, in order to check how the active surface which had developed at the starting temperature, adapted to the new one. As an example, Fig. 2 reports the variation of catalytic performance along with the reaction time for sample with P/V = 0.99, after the equilibrated catalyst had first been operating under the reaction mixture at 440 °C for a few hours, then was cooled down to 380 °C in He, and finally was run with the reaction mixture at 380 °C (Test 3a in Table 1). The progressive slight increase of conversion was accompanied by a more considerable decrease of selectivity to maleic anhydride. After a few hours at 380 °C, the catalyst reached the steady performance. This test indicates that in sample with P/V = 0.99, the active surface at 440 °C is not the same as that one that is stable at 380 °C, and that the former is intrinsically less active but considerably more selective than the latter.

Table 1 summarizes the tests run with the catalyst having P/V = 0.99, and the indications emerged from each test. The most relevant information gained from these experiments is the following:

(1) The active surface that develops under reaction conditions, at 320 °C is similar to that one which forms at 350–380 °C, while it changes when the reaction is carried out above 380 °C. The former active surface performs selectively at moderate temperature, but as soon as the temperature is raised, it gives high conversion but very poor selectivity. At $T > 380$ °C, however, the active surface which develops is moderately active (less active than that one which forms at 380 °C), but much more selective. The transformation of the latter active surface into the former one generates the progressive variation of catalytic performance shown in Fig. 2.

(2) The active surface that develops under reaction conditions at low temperature is not in a fully hydrolysed state, while it is likely oxidized. This picture suggests it to be closer to $VOPO_4$ than to $(VO)_2P_2O_7$ or to a VO_x/polyphosphoric acid mixture. The active surface that develops at high temperature, instead, is hydrolysed and oxidised. This indicates that above 380 °C $VOPO_4$ is hydrolysed to generate a new active surface that is more selective to maleic anhydride.

Table 2 reports some tests carried out with the catalyst having P/V = 1.03. The main indications inferred from these experiments are the following:

(1) The active surface that develops at 320–340 °C is different from that one which forms at 380 °C; specifically, the latter is hydrolysed and partially oxidized. Moreover, it is more active, but equally selective, than the former one. At 340 °C, temperature is too low to initiate the hydrolysis of the VPP, while when the temperature is progressively increased, conditions become more favourable for its hydrolysis, also because of the higher amount of water produced by the reaction. Furthermore, the active phase at 380 °C is not fully oxidized, and the forced development of an higher oxidation state generates an unstable, more selective active surface.

(2) At 440 °C, the active surface is similar to that one which develops at 380 °C.

Therefore, differences at 380 °C between the catalysts having P/V = 0.99 and 1.03 concern the degree of hydrolysis and of oxidation of the active surface. Data suggest that the VPP

Table 2
Description of tests run with catalyst having P/V = 1.03

Test No	Conditions for tests, T and feed[a]	Initial performance in step c[b]	Final performance in step c[b] (time)[c]	Information gained
1b	(a) 380 °C, mix, (b) 380 → 340 °C, in He, (c) 340 °C, mix	X 24, ∅ 73	X 10, ∅ 72, (4 h)	The active surface at 340 °C is different from that one which forms at 380 °C; the latter is more active but equally selective than the former one.
2b	(a) –, (b) 440 °C, in He, 12 h, (c) 440 °C, mix	X 75, ∅ 53	X 76, ∅ 53	The permanence of the active surface in He at 440 °C does not alter its characteristics.
3b	(a) 380 °C, mix, (b) 380 °C, air, 1 h, (c) 380 °C, mix	X 42, ∅ 60	X 40, ∅ 53, (0.5 h)	The oxidation at 380 °C improves the selectivity; therefore, under these conditions the active surface is not fully oxidized.
4b	(a) 380 °C, mix, (b) 380 °C, 4% H_2O in He, 1 h, (c) 380 °C, mix	X 39, ∅ 50	X 40, ∅ 52	The active surface at 380 °C is not altered by a treatment with steam; therefore, at 380 °C the active surface is already hydrolysed.
5b	(a) 440 °C, mix, (b) 440 °C, air, 1 h, (c) 440 °C, mix	X 84, ∅ 59	X 76, ∅ 52, (0.5 h)	At 440 °C, the oxidation improves the performance; therefore, at 440 °C the active surface is not fully oxidized.

[a] (a): Steady performance with the reaction mixture (mix); (b): treatment; (c) unsteady performance with the reaction mixture (mix).

[b] X = n-butane conversion, %; ∅ = selectivity to maleic anhydride, %.

[c] Time necessary to reach the steady final performance in step c, h. If not indicated, the performance was stable all along step c.

in the sample with P/V = 1.03 is less prone to oxidation than the sample having P/V = 0.99, but it undergoes hydrolysis already for low temperatures. This information is in agreement with indications from literature, that excess P stabilizes VPP towards oxidation to $VOPO_4$ [28]. Once the in situ hydrolysis begins, the oxidation of V generates a mixed VO_x/polyphosphoric acid phase, which performs much better than the active surface which develops under the same conditions with the sample having P/V = 0.99, for temperatures between 340 and 400 °C. The latter is essentially made of $VOPO_4$. Therefore, it can be inferred that the hydrolysis of the VPP is the preliminary condition to develop an active surface that performs better than $VOPO_4$. An analogous mechanism of VPP hydrolysis, followed by V oxidation, was proposed years ago by Xue and Schrader [26], who were the first to characterize the VPO catalyst by in situ Raman spectroscopy.

Finally, at high temperature differences between samples become smaller, because the hydrolysis of $VOPO_4$ in sample P/V 0.99, and the further increase of the oxidation level of V in sample P/V 1.03 (under more oxidizing conditions), make the corresponding active surfaces to become similar in the two cases.

Data also indicate that the active surface which performs at best is that one made of $V_2O_5 + P_2O_5/H_2O$ (the latter being a mixture of polyphosphoric species having different condensation degree). This is achieved already at low temperature with catalysts having P/V ratios definitely higher than 1.0; the excess P avoids the formation of $VOPO_4$, while it does favour the hydrolysis of VPP. In sample having P/V = 1.15, this generates an active surface layer with the optimal characteristics in the entire range of temperature, in terms of both hydrolysis and oxidation degree, and hence the best selectivity to maleic anhydride. When instead a P/V ratio close to 1.0 is used, the VPP is easily oxidized to $VOPO_4$ already at low temperature; the latter is hydrolysed to the selective surface layer only at temperatures higher than 380–400 °C.

The results achieved are summarized in Fig. 3, which indicates the approximate range of composition for the active surface. This model also justifies discrepancies in literature concerning the in situ characterization of VPO; in fact, depending on reaction temperature and on catalyst P/V ratio, either an active surface very close to the VPP is identified, or one which is close to $VOPO_4$, or an hydrolysed and oxidised one.

One open question concerns the mechanisms that establish at the catalyst surface, leading to the reversible formation of the different types of active layers, when the reaction temperature is varied (Fig. 1). Variations in the degree of hydrolysis and in the oxidation state of vanadium are likely a function of the gas-phase composition, and of the degree of *n*-butane conversion. For instance, when the hydrocarbon is the limiting reactant, higher oxygen-to-hydrocarbon local ratios at high temperature may favour the development of more oxidised surfaces. This also implies that the nature and extent of transformations illustrated in Fig. 3 are function of the feed composition.

Another question concerns the reasons why a VPP that develops a hydrolysed and oxidised surface gives better selectivity to maleic anhydride, at intermediate and high temperatures, than the intact VPP or $VOPO_4$.

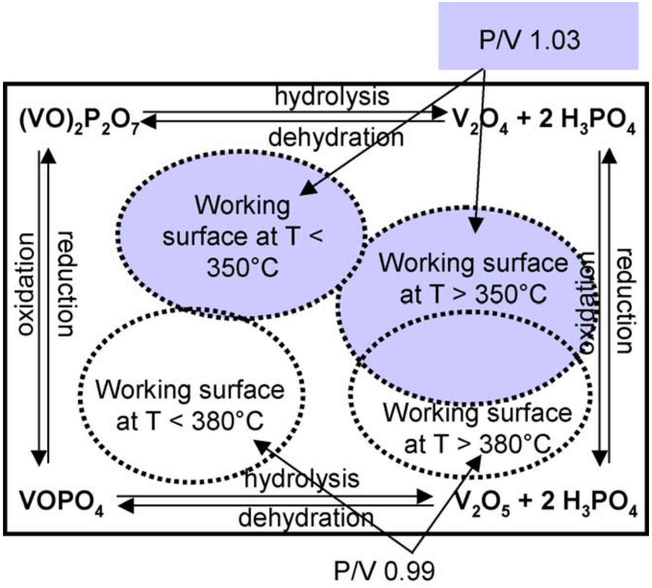

Fig. 3. Scheme summarizing the composition of the active surface for catalysts having P/V ratio equal to 0.99 and 1.03, and for different reaction temperatures. Circled areas represent approximate compositions.

4. Conclusions

The study of the steady and transient performance of equilibrated VPO catalysts having different P/V ratio allowed us to gain information on the nature of the active surface under reaction conditions, during *n*-butane oxidation to maleic anhydride. Specific treatments were applied, and then the transient performance was followed along with the reaction time, until the steady performance was recovered. With the catalyst having P/V = 1.03, the hydrolysis of the VPP surface under working conditions at temperatures higher than 340–350 °C, followed by the oxidation of V, generated an active surface made of vanadium oxide and polyphosphoric acids. When instead the P/V ratio was equal to 0.99, the catalyst surface was oxidized to $VOPO_4$ already at mild temperature, with development of a layer that was very active but unselective at 360–380 °C. At $T > 380$ °C the hydrolysis of $VOPO_4$ led to the development of an active layer similar to that one which forms with the catalyst having P/V > 1.0.

The results obtained explain discrepancies in literature concerning the nature of the active layer in VPO as evaluated by in situ and ex situ measurements; the latter is not only a function of the VPO characteristics (specifically, of the P/V ratio), but also of the reaction conditions.

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