On Surface Phosphorus Activity in VPO Catalysts

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Consideration of the VPO catalyst work usually is focused on vanadium, the agent assumed to be responsible for the electron exchange, while the phosphorus presence if mentioned, generally is not exactly specified. Phosphorus, no doubt, modifies the electronic properties of vanadium atoms, thus, creating suitable catalytic properties. However, the phosphorous role in the electron transfer in the catalyst is still not clear. This paper continues our former study [1], giving additional data on the role of phosphorous in the mechanism of the VPO catalyst work during n-butane oxidation to maleic anhydride.

Samples were the VPO and MLC catalysts. VPO was obtained by known procedure [2,3] with V_2O_5 and H_3PO_4 in n-butyl alcohol. The MLC catalyst (monolayer catalyst) was obtained by the deposition of a vanadium phosphate layer on industrial γ-Al_2O_3 from an organic solution, produced with the use of etoxyphosphite and V_2O_5 [4]. The process was monitored by FTIR and the presence of vanadyl phosphate in the product was confirmed. The XPS analysis based on the peak-to-peak ratio [1] gave the V/Al atomic ratio 0.011, which is less than it was expected (about 0.1) for the monolayer. The catalytic behaviour in direct oxidation of n-butane to maleic anhydride (MA) was tested in a flow microreactor working at 673 K. The feed gas contained 1.5 % n-butane in air. Composition of the effluents was obtained by on-line gas chromatography (MA, n-butane, CO_2).

Phosphorous stability on the surface was studied in another reactor working at the same catalytic conditions. The VPO catalyst was placed on a flat tackle in the stream of reacting mixture at the reaction temperature. Behind it, in the region of decreasing temperature, control plates covered with MgO were placed for deposition of less volatile components carried. The surface composition of these plates was then controlled by XPS. The XPS data handling has already been described [1]. Phosphorous content related to Mg, in a dependence on the distance of plates from the tackle (source of vapours) is shown in Figure 1.

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In [1] we found a mobility of the surface phosphorus and its vapour transport off the reactor. This effect suggests that the catalytic activity is in some way linked with such unstable phosphorus species, and that those lost by volatization can be substituted by other supplied from the bulk. When the bulk is shallow, the catalysis should quickly decay. This hypothesis was verified in the experiment with the MLC catalyst. In this case, the GC analysis started just after the microreactor reached the temperature of the reaction. Results are shown in Figure 2.

The initial activity of VPO catalysts in n-butane oxidation is very often high, but the selectivity is low. During early stages, some solid state processes in catalytic reactor modify the surface of the catalyst, improving the selectivity. In our VPO catalyst, after 175 h of time-on-stream, the catalyst was considered as "equilibrated", *i.e.* conversion at this level should be maintained for a long time. Since then the phosphorous content on the surface did not decrease (Tab. 1), we expected that in this state all losses of an element in the surface composition of the catalysts were compensated by its transport from the environment or from the bulk. Earlier we observed that during the n-butane oxidation on VPO-based catalysts, phosphorus was leaving the surface and for longer time-on-stream the phosphorus depleted region extends inwards [2]. As it was shown [1], phosphorus escapes irreversibly, by vapour transport off the reactor bed. In our experiments it was then bonded on control plates placed in the reactor behind the bed. The amounts of phosphorous deposited there in dependence on the distance from the bed and transport conditions during the deposition are shown in Fig. 1.
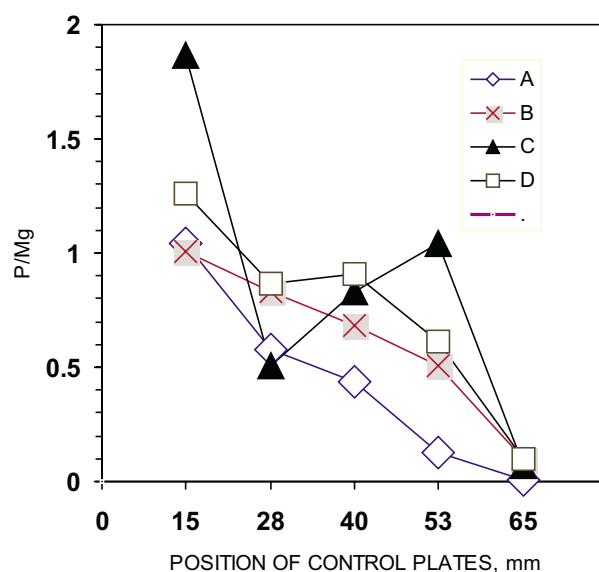

Figure 1. Phosphorus deposited on MgO at different distances from the bed of VPO catalyst during the oxidation of n-butane to maleic anhydride at 673 K. A) reagents space velocity (sv) 20 cm^3/min, time of transport (t) and deposition (d) 5 h; B) sv = 20 cm^3/min, t = d = 15 h; C) sv = 10 cm^3/min, t = 160 h, d = 15 h; D) sv = 10 cm^3/min, t = d = 15 h.

Region of its deposition, restricted to less than 70 mm and above 473 K, suggests that the carrier compound was not very volatile. Phosphorus oxides or related acids are able to vaporize even at room temperature and they can very easily react with MgO. Pentoxide sublimates at this temperature, but water produced in the catalytic reaction can easily transform it to phosphoric acids, which are also volatile. Sesqui hydrate $H_3PO_4 \cdot 1.5\ H_2O$ at 25°C exhibits the vapour pressure p = 0.85 Tr [5,6]. Since XPS in this circumstances is sensitive enough to detect even traces of a phosphoric acid, it seems also likely that phosphorus can be carried out off the catalyst bed as an acid or an organic compound.

Data obtained under higher space velocity (20 cm^3/min) and short time of transport and deposition suggested a more or less monotonic decay in concentration of a phosphorous compound with distance and decreasing temperature (A and B in Fig. 1). However, with space velocity (10 cm^3/min) shorter by twice (longer the vapour-MgO contact time) an amount of the deposited phosphorus clearly passes by maximum corresponding to the distance of about 40 mm from the source (C and D in Fig. 1). Such effect can be the result of the presence of two different chemically vapour species. The second form seems to be more volatile and is reacting at lower temperature. Chemical transformation of a primary volatile phosphorus compound in the gaseous reaction products (*e.g.* hydrolysis) is also possible.

XPS data show (Tab. 1) that the VPO catalyst in spite of a long vapour transport, after 160 h of the time-on-stream at the surface contained a little more of phosphorus than before work.

Table 1. Binding energies and surface compositions in the VPO catalyst

Surface	V 2p3/2, eV	P2p, eV	Atomic ratios	Remarks
Catalyst VPO 1a	517.0	133.4	P/V = 1.46	before work
Catalyst VPO 1b	517.2	133.6	P/V = 1.53	after 160 h work
Catalyst MLC	517.5	134.0	V/Al. = 0.011	

Since during very long time-on-stream the subsurface region of the catalyst becomes depleted with phosphorus [2], both these observations lead to the conclusion that in the catalytic process phosphorus all time is transported from the bulk to the surface and then, by vapour phase, is carried off the catalyst bed. An intriguing question appears, to what extent this stream is connected with the ability to perform the catalytic transformation.

The experiment with the monolayer VPO catalyst has brought some light into this question. In the preparation course of the MLC catalyst, amount of vanadyl-phosphate was so chosen that in the final product it did not covered the whole surface of the Al_2O_3 carrier. XPS analysis gave the ratio V/Al = 0.011, suggesting that the condition wanted of less than one monolayer coverage by vanadyl-phosphate should be fulfilled.
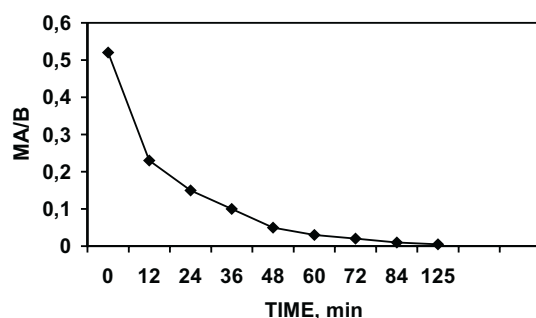
Figure 2. Maleic anhydride yield on the MLC catalyst.

The catalytic test with the MLC catalyst started immediately after the system reached the reaction temperature. Results presented in Fig. 2 show that the selectivity to maleic anhydride high initially, had been quickly quenched. Such an easy lost of the ability to oxidize n-butane molecules can be simply explained. In the case of the catalyst monolayer, the active phase is quickly decomposed, due to phosphorus transport out of the catalyst bed. But unlike the bulk catalyst, in the case of a monolayer, the compensation of the phosphorus losses could not proceed, because the bulk is not present.

Finally it can be concluded, that during the catalytic oxidation of n-butane to maleic anhydride, phosphorus is very slowly transported out of the catalyst bed. It is likely carried out by one or two volatile species. They can be phosphorus acid and/or an organic compound able to hydrolyse, releasing free molecules of the phosphoric acid. The phosphorous losses on catalyst surface can be easily compensated by overstochiometric or lattice phosphorus species transported from the bulk.

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