



# Transient behavior of vanadyl pyrophosphate catalysts during the partial oxidation of *n*-butane in industrial-sized, fixed bed reactors



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## ABSTRACT

The industrially important application of vanadium phosphorus oxide catalysts is the partial oxidation of *n*-butane in multi-tubular fixed bed reactors. Despite many decades of investigation about the functionality of the catalyst, the reaction mechanism is still under debate. However, the loss of phosphorus from the catalyst as a technically important phenomenon was until now hardly considered in the scientific literature: this phosphorus loss during long term operation has a strong effect on the temperature distribution in the reactor, which in turn significantly affects the catalyst selectivity. Therefore, technical reactor operation usually requires the addition of ppm levels of an organic phosphorus compound together with water to the reactor feed. For a macro-scale investigation of the phosphorus dynamics, the present study reports elaborated experiments in an industrial scale fixed bed reactor. The experiments revealed significant changes in catalyst activity and reactor performance induced by only minor variations in the feed contents of phosphorus and water as function of butane feed and space velocity, as well as strong interactions between these two additional feed components. These observations are further related to the many literature reports about the active catalyst surface. Common aspects explaining the dynamic catalyst behavior were combined in a new scheme for the VPP/VPO surface chemistry.

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## 1. Introduction

Maleic anhydride (MA) is an important intermediate in the chemical industry. It is produced by selective catalytic oxidation of *n*-butane with air over vanadium phosphorus oxide (VPO) catalysts. Commercially, this reaction is mainly carried out in multi tubular fixed bed reactors filled with shaped catalyst particles. Such reactors can include around 30,000 tubes of 21–25 mm diameter and 3–6 m length [1]. The reaction heat is removed by molten salt at temperatures around 400 °C, while feed concentrations are restricted to below 2 vol% *n*-butane due to limited heat transfer properties of the reactor. Main byproducts are CO and CO<sub>2</sub> which are formed by parallel and consecutive reactions, according to a triangular reaction network. Other byproducts are acrylic and acetic acid which are observed in minor amounts [2,3].

A number of patents reveal an important aspect of the commercial application of VPO-catalysts for the production of maleic anhydride from *n*-butane [4–8]. Apparently, the catalyst performance declines with time as its selectivity decreases with

simultaneously increasing activity. As a consequence the MA yield diminishes and the reactor operation shifts towards less stable regions. Because of the general assumption that a loss of phosphorus from the catalyst is responsible for this unwanted behavior [3,7], a variety of technologies are claimed compensating this loss in order to ensure optimum operation of commercial reactors. This implies the addition of an organic phosphorus compound, such as trimethyl phosphate (TMP), to the reactor feed. Furthermore, the addition of water seems to play an important role for an adequate distribution of phosphorus in the catalyst bed [5,6].

Although reaction mechanism and nature of the active vanadium phases on the VPO surface have been debated for decades, they are still not fully resolved. Several faces of the vanadium pyrophosphate crystals and different redox couples have been proposed, while during the last decades different orthophosphate species and their role in the reaction mechanism were discussed [9–20]. A particular subject of the debate however, is the theory that a highly dynamic surface forms on the vanadium pyrophosphate (VPP) precursor under reaction conditions, which is composed of various VPO phases [13,14,21] as a function of operating conditions. With respect to the phosphorus issue in the commercial application, an important aspect of this view on the catalyst surface is the role of water during these dynamic changes. It is assumed that

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water promotes the formation of surface phosphates which in turn may be released to the gas phase [21–24].

Regarding the relation between phosphorus content and catalyst performance it is generally assumed that excess phosphorus prevents the oxidation of VPP ( $V^{4+}$ ) to  $V^{5+}$ -species [9,13,25,26] which often have been detected under reacting conditions [13–16]. On the other hand, an irreversible loss of phosphorus was related to catalyst deactivation by formation of  $V_2O_5$  [27]. Selectivity too was found to depend on the P/V ratio of the catalyst [10,11,13,14]. Important, more recent works on this topic are those of Cavani et al. [13,14], who found varying surface compositions with different activity-selectivity relationships as a function of P/V ratio and reaction conditions.

From a variety of *in situ* analyses of the working VPO surface it was additionally concluded that structure and composition of the active VPO surface vary as a function of reaction conditions [13,14,21–24,28]. A significant enrichment of phosphorus on the surface is an important observation [21–23]. Further, the influence of water, which is always present as a reaction product, on the surface dynamics is strongly related to these findings. On the one hand, water was found to reduce reaction rates and to affect the selectivity by adsorption on surface sites [29–31]. On the other hand, water was reported to facilitate re-oxidation of the catalyst [22,23,32], and to promote the formation of separated phosphate species on the surface [21,24], which is in turn related to the phosphorus enrichment [22,23]. The works of Cavani et al. [13,14] additionally

suggest a direct influence of water on the appearance of different orthophosphates.

Debating the role of water for the mobility of phosphorus in the catalyst, Cavani et al. [13] proved its ability to remove phosphorus from the catalyst by treating the catalyst with water. This finding hence is directly related to the conclusion of patent literature that the addition of water is necessary for an adequate distribution of phosphorus in the catalyst bed [5,6].

However, beyond the information provided by patents, scientific literature could not be found on more precise investigations with respect to the addition of phosphorus to fixed bed reactors. In the area of micro-scale reactor studies [13,22], there are only a few studies which touch this subject. In addition, the operating conditions which were typically applied in laboratory reactors generally permit long-term operation without significant changes of the catalyst activity [33].

In this work, elaborated experiments in an industrial scale fixed bed pilot reactor are presented during which the influences of phosphorus and water on the transient reactor behavior were studied. To this end, a commercial VPO catalyst was used provided by Clariant AG. The experimental observations are discussed in the frame of the apparently contradictory debates in the scientific literature about the functionality of the VPO surface during *n*-butane oxidation.

Throughout the presented work the following definitions account:

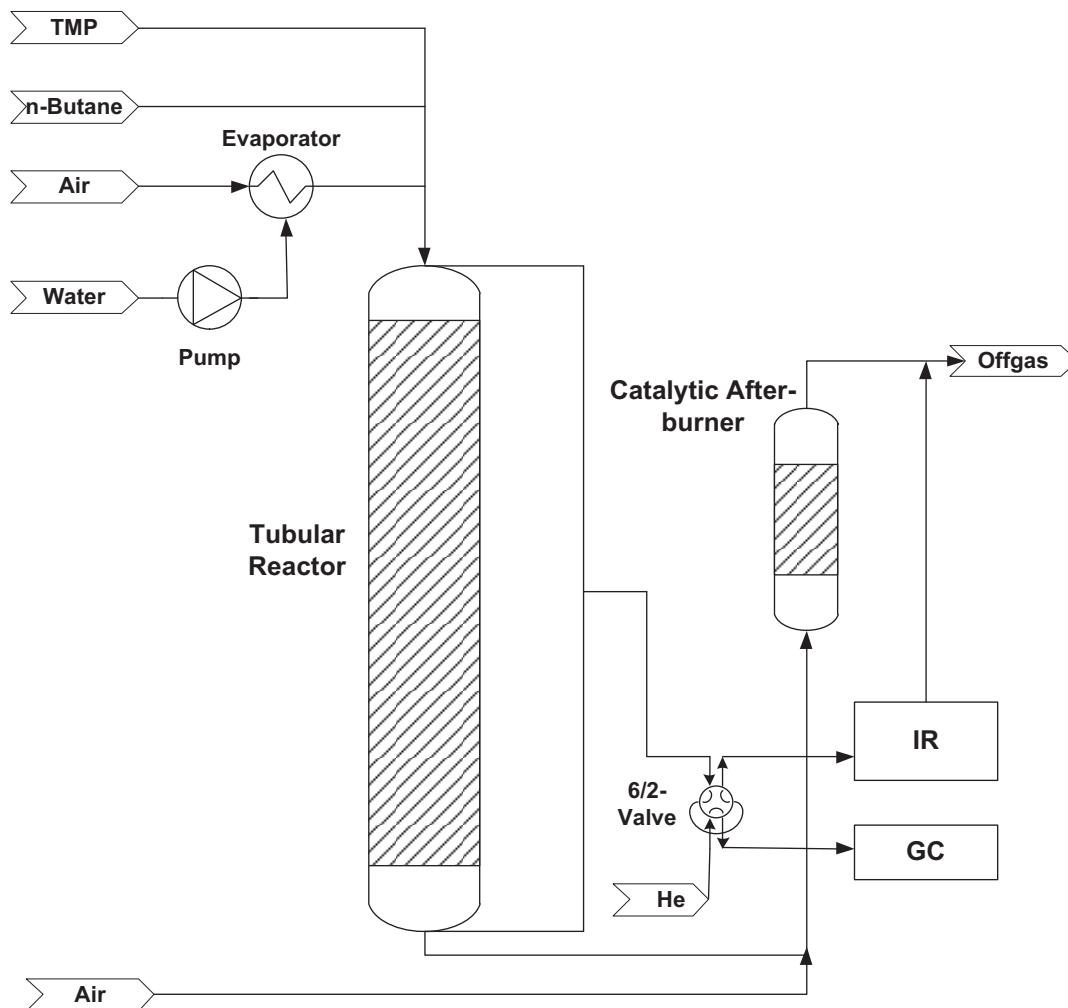


Fig. 1. Process flow diagram of the pilot reactor.

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