# Structural characteristics of an amorphous VPO monolayer on alumina for propane ammoxidation

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## ARTICLE INFO

## ABSTRACT

The structural properties and oxidation state of vanadium in alumina-supported vanadium-phosphorous oxides at nearly monolayer coverage influence its catalytic performances. The population distribution $V^V$=O and $V^{IV}$=O species in the amorphous VPO phase strongly depends on the sample history. By using alumina-supported VPO instead of conventional bulk catalysts, we facilitate enhanced discrimination between active phase and bulk phase signals in the vanadium-phosphorous oxygen system. This brings light on the speciation of VPO catalysts in general. Our observations were achieved by using mainly in situ EPR & *operando* Raman–GC spectroscopic techniques at relevant temperatures and gas conditions, showing that the $(V^{iv}O)_2P_2O_7$ phase is formed during propane ammoxidation at 753 K. Such transformation is less intense in inert atmosphere at 753 K. Ammonia adsorption on the VPO catalyst surface leads to the formation of $VO^{2+}$ sites, probably bearing Brønsted and/or Lewis acidity. Propane ammoxidation appears to promote the formation of mixed valence compounds.

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## 1. Introduction

Vanadium phosphorous oxides (VPO) have been used as catalysts for selective oxidation reactions for several decades [1], being the objective of extensive research, and they are widely used in industry. The presence of a plethora of crystalline and amorphous vanadium phosphate phases makes the deduction of rational relationships between structure and reactivity a tremendous task [2–6]. An alumina-supported VPO based catalyst ($VPO/Al_2O_3$) for propane ammoxidation is a potentially interesting catalytic system for industrial synthesis of acrylonitrile. It is also an excellent model system for the study of the speciation of the complex VPO catalysts with spectroscopic techniques. This is because the signals from the bulk oxide (support) usually dominate the acquired spectra, except when true surface probing methods are implemented, e.g. LEIS [7], though these may not provide molecular information but just deliver information on the outermost layer composition. In bulk VPO catalysts, the reaction environment modifies both the bulk lattice and the surface layer of the catalyst [1,8]. However, in these systems, the signal from the support (bulk phase) will overlap with that of (outermost layers of) the supported phase. Thus, to avoid or at least minimize the interference from the bulk phase, the surface-to-volume ratio can by enhanced by synthesis of supported

nanoscaled catalysts [9,10]. For example, the catalytic performance of surface vanadium and phosphorus oxide species on titania has been shown to be similar to that of bulk VPO during butane oxidation [11–13]. The idea is outlined for the case of a supported VPO catalyst in Fig. 1. The sub-monolayer, near monolayer (or amorphous layer) supported VPO catalyst as well as a complete bulk VPO catalyst are sketched.

The active surface for propane to acrylonitrile oxidation has earlier been shown to contain the vanadyl pyrophosphate phase, $(VO)_2P_2O_7$ (VPP) [14,15]. This is a general feature for VPO based catalysts, and the structure of $(VO)_2P_2O_7$ single crystals has been determined by X-ray methods: it consists of layers of edge sharing pairs of $VO_5$ units linked by pyrophosphate groups [16]. Furthermore, surface-sensitive studies reveal the presence of vanadyl groups, V=O, and Lewis acid sites at the surface [17]. The distribution of the VPO phases, and thus the catalytic properties, depends on the preparation methods, catalysts precursor and reaction conditions. The industrially employed VPO catalyst for n-butane oxidation mainly contains the vanadium pyrophosphate phase, but the presence of an amorphous overlayer of $VOPO_4$ type phase increases the catalyst activity and selectivity to maleic anhydride [18]. Thus, vanadium $V^{4+}$ and $V^{5+}$ sites as well as the above-mentioned Lewis acid sites [17], have been proposed as active sites in n-butane oxidation to maleic anhydride [12]. The presence of defects within the VPO phases has been related to the red-ox properties of the catalysts and has been reported to activate alkanes [19–21]. These complexities and the dependency of
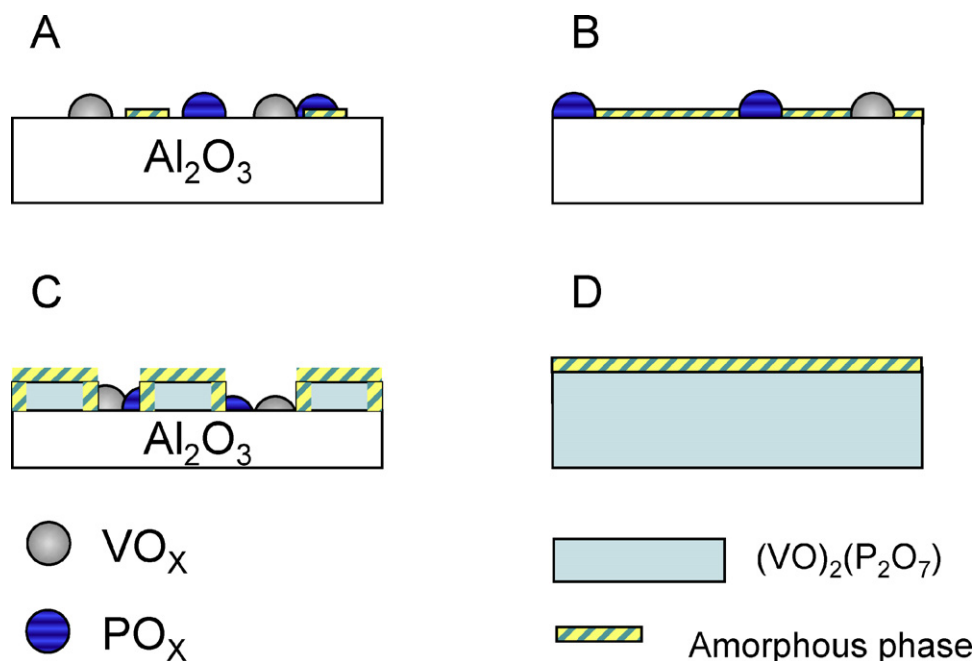
**Fig. 1.** Principal sketch of how different V + P amounts impregnated on an alumina support will influence the formation of possible VPO phases. (A) Sub-monolayer (with respect to phosphor) supported catalyst, (B) a near monolayer VPO catalyst on an alumina carrier, (C) overloaded and (D) complete bulk VPO catalyst.

material properties on the synthesis method have lead to contradictory interpretations in the literature. According to Cavani et al., the numerous contributions reporting the properties of VPO catalysts only at the laboratory scale and in specific ex situ measurements, have created even confusion [22]. In this work we show by in situ spectroscopic measurements how a non-crystalline VPP phase on alumina constitutes an active catalytic system. We follow the behavior of the stabilized, amorphous $N_2$ activated VPO phase by high-temperature EPR and Raman spectroscopy on fresh precursor and pre-treated samples. These techniques evidence changing equilibria between $V^{5+}$ and $V^{4+}$ moieties, until a final active catalyst is formed at the operation temperature. Thereafter, the state of the active phase is followed by Raman spectroscopy during catalytic reaction. Bentrup et al. [23,24] studied the $V_2O_5$- and $V_2O_5$-$Sb_2O_3$/$TiO_2$ systems and found by *operando* EPR spectroscopy, combined with FTIR and UV–vis spectroscopic measurements, that vanadium reduces to V(IV) and further down to V(III) during butane oxidation at 453–473 K. Similarly, an in situ EPR study of bulk $(VO)_2P_2O_7$ catalysts used for selective oxidation of p-substituted toluenes showed that the substrate type influences the EPR signal by perturbation of the spin–spin exchange. Though convincingly done, their experiments (notably during the *operando* EPR measurements) were dominated by the continuous presence of bulk $(V^{iv}O)_2P_2O_7$ during their cycling between inert and feed gases.

In situ investigations with conventional methods are complex because the catalytic chemistry takes place in an amorphous phase, and the nature of both the carrier and the dark amorphous VPO phase makes difficult the investigation using directly conventional spectroscopic methods based on absorption or emission of light. However, EPR spectroscopy is in this case a very useful tool. This is because the alumina carrier is "EPR silent", which means that no paramagnetic species are present in the carrier and the long wavelength (radio waves) allows the electromagnetic waves to penetrate the carrier, thus enabling direct monitoring of the active phase of the catalyst. Furthermore, since $VO^{2+}$ exhibits resolved spectra even at elevated temperatures, valuable information of the V(IV) content and its coordination can be obtained.

## 2. Materials and methods

### 2.1. Synthesis of VPO/Al₂O₃ catalysts

Vanadium and phosphorous were supported on γ-alumina by the incipient wetness impregnation method to yield a total coverage of 8 V atoms $nm^2$ and 9 P atoms $nm^2$ (from now on denoted 8V9PAl) on the alumina support. This is in the order of two monolayers of V + P on the oxide support. The precursor of $(VO)_2P_2O_7$ was formed in situ by dissolving oxalic acid (6.5 g, Panreac Química S.A.) and ammonium metavanadate (3.25 g, 99%, Sigma–Aldrich) in 8 ml of distilled water. The solution was stirred one hour at 343 K and phosphoric acid (3.47 g, 85%, Panreac Química S.A.) was added. The final solution was stirred at 343 K and, after one hour, impregnated over 10 g of γ-alumina by incipient wetness impregnation method. The catalyst was then dried and one sample pre-activated for 19 h in $N_2$ flow at 673 K.

### 2.2. In situ Raman spectroscopy

Raman spectra were acquired with a single monochromatic Renishaw System 1000 equipped with a cooled CCD detector and an Edge filter. The samples were excited with the 488 nm Ar line, with a power of 0.9 mW, under reaction conditions in a home-made reaction cell. The low power used renders any heat effect from the laser negligible. The spectral resolution was 3 cm$^{-1}$, and the spectrum acquisition was 150 s for each sample. The catalyst was previously activated at 673 K in a nitrogen flow for 19 h. $O_2$, $NH_3$, $C_3H_8$ and He feed, preheated up to 473 K, was supplied and controlled using Bronkhorst flow controllers. The total flow was 20 ml min (GHSV: 3000 h$^{-1}$ approximately) corresponding volumetrically to 25% of $O_2$; 9.8% of $C_3H_8$; 8.6% of $NH_3$ and 56.6% of He. The main test was made using 0.2 g of catalyst with a particle size of 850–1000 μm on a set of samples previously investigated by *operando* Raman-GC using the 514 nm Ar$^+$ line [15], but with smaller particle size distribution (125–250 μm). For comparison, an extract of these *operando* data are reported here as well. While acquiring the Raman spectra, the activities of the catalyst samples were verified with an on-line gas chromatograph, Varian CP