

# Cr, Mo and W used as VPO promoters in the partial oxidation of *n*-butane to maleic anhydride

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## Abstract

The present work addresses the issue of the promoter effect produced by group VIB elements added to the basic VPO formulation using different methods and loads in order to obtain information linking the catalytic behavior of the solids with their physicochemical properties. The unpromoted VPO precursor ( $\text{VOHPO}_4 \cdot 1/2\text{H}_2\text{O}$ ) was prepared from  $\text{V}_2\text{O}_5$  reduced with an alcoholic mixture and 100%  $\text{H}_3\text{PO}_4$ . Cr, Mo or W were either impregnated on the VPO precursor or co-precipitated during the precursor synthesis. The precursors containing varying loads of the promoter were activated following a standard procedure in the same flow micro-reactor where the catalytic performance was evaluated. The precursors and the catalysts were characterized by X-ray diffraction (XRD) and laser Raman spectroscopy (LRS). Acetonitrile was used as a probe molecule to test the strength of the Lewis acid sites monitored by FTIR. The amount of chemisorbed acetonitrile was measured in a standard high vacuum system. The addition of the promoters invariably increased the catalytic activity but in every case there was an optimum load to achieve the best selectivity. The origin of this maximum could be ascribed to the right balance between the presence of very strong Lewis acid sites and the development of  $\text{V}^{5+}$  isolated sites in the matrix of the vanadyl pyrophosphate, by far the major crystalline phase present in the catalyst. The three group VIB promoters affect the balance between acid and redox properties but increase the overall activity in all cases.

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## 1. Introduction

The mixed phosphorus and vanadium oxide known as VPO is the only system capable of oxidizing *n*-butane to maleic anhydride with good selectivity. Promoters are added to industrial formulations to improve both catalytic properties and mechanical resistance. A long list of elements has been tested but the exact role of each element is mostly unknown and controversial.

Different authors have stressed a variety of aspects concerning the role of promoters such as the mode of addition [1], the load [2], the promoter electronegativity [3], the generation of defects [4], the redox character [5] and acidity [6,7]. Other authors have speculated on the formation

of a solid solution, based on the fact that molybdenum phosphate ( $\text{MoOPO}_4$ ) and  $\text{VOPO}_4$  are iso-structural phases and, consequently, it is possible that during the stabilization period a small amount of a solid solution of Mo and V mixed phase could have been formed [8]. More recent studies have used Mo in combination with other dopants (Zn, Zr) added by impregnation. Besides, in order to increase the surface area the precursors were ball milled [9].

Note that commercial catalysts always have P/V ratios slightly higher than one. Another alternative would be that the added metal forms some amorphous phase with excess phosphorus decreasing the loss of this element by sublimation, which requires its permanent replenishment in industrial practice [8]. Mc Cormick et al. [10] have proposed that a possible role of the promoter would be to accelerate the rate of  $\text{V}^{5+}$  phase formation to yield the neighboring  $\text{V}^{5+}/\text{V}^{4+}$  couples required in the Mars and van

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Krevelen [11] type of mechanism proposed for several steps of the overall reaction.

From a mechanistic viewpoint, it is well known that the hydrogen abstraction is the rate-determining step both in an olefinic and in an alcoxide mechanism [12–14]. A suitable candidate to favor the hydride abstraction is a strong Lewis site. According to Centi et al. [12], this site could be a  $V^{4+\delta+}$  site stemming from defects in the structure of the vanadyl pyrophosphate [2 0 0] plane or, as suggested by Volta and co-workers, it could be a  $V^{5+}$  center either dispersed in the same phase or from a  $VOPO_4$  phase [4,13,14].

The present work addresses the promoter effect produced by chromium, molybdenum and tungsten which have been added using different methods and loads in order to obtain information linking catalytic behavior of the solids with their physicochemical properties. These elements were selected because, similarly to V, they have a “d” character, various oxidation states under reaction conditions, their oxides are acidic and they could possibly form intercalation or substitution compounds with vanadium. Moreover, these elements are used in the oxidehydrogenation of short-chain paraffins where their main role is to accelerate the rate-determining step of C–H bond breaking [15,16].

## 2. Experimental

### 2.1. Precursor synthesis

The precursor was obtained by reduction of 5 g of  $V_2O_5$  with 30 ml of isobutyl alcohol and 20 ml of benzyl alcohol under reflux for 3 h. Orthophosphoric acid 100% was then added in the amount needed to obtain a P/V ratio of 1.3 and the solution refluxed for another 2 h. After completion of the reaction, the solid phase was recovered by filtration and dried in an oven at 150 °C overnight. The solid obtained was the VPO catalyst precursor (with no promoter added). Two types of promoted catalysts were prepared: (i) impregnated and (ii) co-precipitated. In order to prepare the impregnated formulations, the necessary amount of isobutyl alcohol solution of the corresponding salt was incorporated to the VPO precursor by incipient wetness technique. In the case of co-precipitated solids, the salt containing the promoter was also dissolved in isobutyl alcohol and added to the system in the phosphatation step together with the phosphoric acid.

A VPO(a) base was prepared to impregnate Mo with 1.0, 3.0 and 5.0% and a second VPO(b) base was also prepared for the impregnation of Cr and W, yielding catalysts impregnated with 0.5, 1.0 and 1.5% Cr and with 1.7, 3.5 and 10.5% W. The co-precipitated catalysts had 1.0 and 5.0% Mo; 1.0, 1.5 and 3.0% Cr and 2.5, 5.0 and 10.5% W. The nomenclature used is *M*/%/*x*, to indicate promoter name/metal% by weight/*x*: preparation method, where *i*: impregnation and *c*: co-precipitation. The promoter concentrations were calculated through a mass balance made taking into account the amount of reactants used in the preparation. This

is justified by the fact that the promoter salts accurately weighted are fully incorporated in the precursor with no residues left out.

### 2.2. Catalyst activation and testing

A fixed-bed reactor containing 1.0 g of precursor with particle size in the range of 177–250 microns was used to activate the solids and perform the catalytic tests. *n*-Butane and maleic anhydride were analyzed using an on-line gas chromatograph equipped with an FID detector and an AT-1200 column. The precursor was activated as follows: while flowing the reactant mixture (1.5% *n*- $C_4H_{10}$  in air) at GHSV = 900  $h^{-1}$ , the solid was heated at 3 °C  $min^{-1}$ , up to 280 °C, kept at this temperature for 3 h and heated again to the temperature needed to achieve 80% conversion (~380 °C). The system was kept under reaction conditions until no variation in both conversion and selectivity occurred (usually 48 h). At this point, the catalyst reached the steady state to measure its catalytic performance by varying temperature and space velocity as needed.

### 2.3. Precursor and catalyst characterization

#### 2.3.1. Surface area

It was measured by  $N_2$  adsorption (BET method) using a Quantachrome Nova 1000 sorptometer.

#### 2.3.2. X-ray diffraction (XRD)

The measurements were made with a Shimadzu XD-D1 X-ray diffractometer, using nickel-filtered  $Cu K\alpha$  radiation with a scanning rate of 1°  $min^{-1}$ .

#### 2.3.3. Laser Raman spectroscopy (LRS)

The Raman spectra were recorded with a Jasco laser Raman spectrometer model TRS-600-SZ-P, equipped with a charge coupled device (CCD) with the detector cooled to about 153 K using liquid  $N_2$ . The excitation source was the 514.5 nm line of a spectra 9000 photometrics Ar ion laser. The laser power was set at 40 mW. The powdered solid was pressed as a thin wafer about 1 mm thick, and all the spectra were recorded with the samples under ambient conditions.

#### 2.3.4. Fourier transform infrared spectroscopy

The IR spectra were obtained using a Shimadzu FT-IR 8101M spectrometer with a spectral resolution of 4  $cm^{-1}$ .

#### 2.3.5. Acetonitrile adsorption

The samples for the adsorption experiments were prepared by compressing the used catalysts at 4 tonnes  $cm^{-2}$  in order to obtain self-supporting wafers. They were mounted on a transportable infrared cell with  $CaF_2$  windows and external oven. The pretreatment was performed in a high vacuum system. The sample was first outgassed at 450 °C for 12 h in a dynamic vacuum of  $1.0 \times 10^{-5}$  Torr. After cooling to room temperature, a spectrum of the catalyst

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